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ABSTRACT

THERMOCHEMISTRY AND BOND ENERGIES OF NITRO -ALKANES, -ALKENES, -CARBONYLS AND CORRESPONDING NITRITES

by
Suarwee Snitsiriwat

Density functional and ab initio theory based calculations were performed on a series of nitro -alkanes, -alkenes, carbonyl and corresponding nitrites representing large-scale primary, secondary and tertiary nitro compounds and their radicals resulting from the loss of skeletal hydrogen atoms. Geometries, vibration frequencies and thermochemical properties, $\Delta_f H^\circ_{298}$, $S^\circ(T)$ and $C^\circ_p(T)$ ($10\text{K} \leq T \leq 5000\text{K}$) are calculated at the individual B3LYP/6-31G(d,p), B3LYP /6-31+G(2d,2p) and composite CBS-QB3 levels. Potential energy barriers for the internal rotations have been computed at the B3LYP/6-31G(d,p) level of theory and the lower barrier contributions are incorporated into entropy and heat capacity data. The standard enthalpies of formation at 298 K are evaluated using isodesmic reaction schemes with several work reactions for each species. Recommended values derived from the most stable conformers of respective nitro- and nitrite isomers include: -30.6 and -28.4 kcal mol⁻¹ for *n*-propane-, -33.9 and -32.3 kcal mol⁻¹ for *iso*-propane-, -42.8 and -41.4 kcal mol⁻¹ for *tert*-butane-nitro compounds and nitrites, respectively. Entropy and heat capacity values are also reported for the lower homologues: nitromethane, nitroethane and corresponding nitrites. C—H bond energies are decreased by ~ 5 kcal mol⁻¹ alpha to the nitro or nitrite groups and increased by ~ 0.5 kcal mol⁻¹ beta to the nitro and nitrite groups.

Recommended values for enthalpies of formation of the most stable conformers of nitroacetone, acetonitrile, nitroacetate and acetyl nitrite are $-51.6 \text{ kcal mol}^{-1}$, $-51.26 \text{ kcal mol}^{-1}$, $-45.4 \text{ kcal mol}^{-1}$ and $-58.2 \text{ kcal mol}^{-1}$, respectively. The calculated $\Delta_f H^\circ_{298}$ for nitroethylene is $7.6 \text{ kcal mol}^{-1}$ and for vinyl nitrite is $7.2 \text{ kcal mol}^{-1}$. The carbonyl and olefin groups retain the major influence on the C-H bond energies. Radicals on carbon adjacent to a nitrite (RC.ONO) group do not exist; they dissociate to the corresponding carbonyl (RC=O + NO) with 38 kcal mol^{-1} exothermic and no apparent barrier. This results from formation of the strong carbonyl (π bond $\sim 80 \text{ kcal mol}^{-1}$) with dissociation of the weak RO—NO bond ($\sim 43 \text{ kcal mol}^{-1}$).

**THERMOCHEMISTRY AND BOND ENERGIES OF NITRO -ALKANES,
-ALKENES, -CARBONYLS AND CORRESPONDING NITRITES**

**by
Suarwee Snitsiriwat**

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Master of Science in Environmental Science**

**New Jersey Institute of Technology and Rutgers,
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APPROVAL PAGE

**THERMOCHEMISTRY AND BOND ENERGIES OF NITRO -ALKANES,
-ALKENES, -CARBONYLS AND CORRESPONDING NITRITES**

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Work like you don't need money,
Love like you've never been hurt,
Sing as if no one can hear you,
And dance like no one's watching.

Anonymous

It takes twenty years to make an overnight success.

Eddie Cantor

There are no rules of architecture for a castle in the clouds.

G.K. Chesterton

You may be disappointed if you fail, but you are doomed if you don't try.

Beverly Sills

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CHAPTER 1

THERMOCHEMICAL PROPERTIES FOR N-PROPLY, ISO-PROPYL AND TERT-BUTYL NITROALKANES AND ALKYL NITRITE

1.1 Objective

Density functional theory based calculations are performed on a series of alkyl nitrites and nitroalkanes representing large-scale primary, secondary and tertiary nitro compounds and their radicals resulting from the loss of skeletal hydrogen atoms. Geometries, vibration frequencies and thermochemical properties, $\Delta_f H^\circ_{298}$, $S^\circ(T)$ and $C^\circ_p(T)$ ($10\text{K} \leq T \leq 5000\text{K}$) are calculated at the individual B3LYP/6-31G(d,p), B3LYP/6-31+G(2d,2p) and composite CBS-QB3 levels. Potential energy barriers for the internal rotation have been computed at the B3LYP/6-31G(d,p) level of theory and the lower barrier contributions are incorporated into entropy and heat capacity data. The standard enthalpies of formation at 298 K are evaluated using isodesmic reaction schemes with several work reactions for each species. Recommended values derived from the most stable conformers of respective nitro- and nitrite isomers include: -30.57 and -28.44 kcal mol⁻¹ for *n*-propane-, -33.89 and -32.32 kcal mol⁻¹ for *iso*-propane-, -42.78 and -41.36 kcal mol⁻¹ for *tert*-butane-nitro compounds and nitrites, respectively. Entropy and heat capacity values are also reported for the lower homologues: nitromethane, nitroethane and corresponding nitrites.

1.2 Background Information

Accurate formation enthalpies, $\Delta_f H^\circ_{298}$, for the simplest nitro and nitrite molecules are required in order to understand reaction paths and assist in the development of detailed chemical kinetic mechanisms. In turn, these mechanisms can be applied to model the formation and destruction of nitrogen species in a variety of environments, particularly for atmospheric and combustion chemistries. Since less than 0.02% of known organic species have had their heats of formation measured¹ the application of modern quantum chemistry methods for this data is of value, provided that reasonable accuracy can be obtained. The establishment of these basic values will also aid in the determination of the thermochemical properties of higher homologues *via* use of isodesmic reactions with group conservation (isogeitonic reactions). This study continues development and evaluation of thermochemical properties on simplest nitro- and nitrite compounds from our previous analysis.^{2,3}

Nitro (RNO_2) and nitrite (RONO) derivatives of hydrocarbons undergo thermal decomposition at relatively low temperatures and hence have potential as both propellants and energetic materials: the reaction barriers for bond cleavage of R-NO_2 (alkyl nitro compounds) and RO-NO (corresponding nitrites) are *ca.* 61 and 40 kcal mol⁻¹, respectively.⁴⁻⁸ The nitro alkanes and alkyl nitrites can release NO and NO_2 and hence can serve as catalysts in oxidation of hydrocarbons.⁹⁻¹¹ In this regard, nitro compounds have been widely studied by both experimental and theoretical methods,^{4-8, 12-33} nevertheless, the thermochemical data are surprisingly limited.

Decomposition of the simplest nitro alkanes as prototype models for larger monopropellants has been the subject of numerous studies.^{1, 4-8, 13-17, 21-26} For nitroethane,

the concerted elimination of HONO *via* a five-centered intermediate is the lowest energy decomposition channel according to the BAC-MP4 and B3LYP/6-311+G(3df,2p) calculations.¹⁶ Estimated DFT barriers for nitroethane and 2-nitropropane (42.0 and 39.2 kcal mol⁻¹, respectively) are comparable to the experimental activation energy data of Benson and co-workers of 43.0 and 42.0 kcal mol⁻¹.²⁶

Conformational aspects of alkyl nitro compounds, in particular *syn-anti* equilibrium have been studied by several researchers.^{13, 19, 30} These results show that R-skeletal groups mainly destabilize sterically favored *syn* conformers. The magnitude of the steric forces has been shown to correlate with relative stabilities data from ¹H NMR on primary alkyl nitrites.³⁰ For *iso*-alkyl nitrites, the reverse order was obtained as it was expected. Theoretical models also confirm the stability of *syn* conformers.^{13,19}

In the present work, we have evaluated the formation enthalpies of several *n*-alkyl nitro compounds bearing -ONO (nitrite) and -NO₂ (nitro-) moieties in typical primary, secondary and tertiary positions based on their most stable rotation conformers using multilevel and individual computational chemistry methods. We used both complete basis set and Gaussian composite calculation methods. These methods employ a variety of different geometries, frequency determinations and higher order energy corrections (*vide infra*). The accuracy of these methods has been demonstrated in our previous studies on HONO isomers² and methyl and ethyl nitro and nitrite compounds.³

Ashcraft and Green et al.⁴⁹ have recently reported thermochemical properties and group values for several nitrogen-containing, stable molecules in this study with CBS-QB3 based atomization method with included spin-orbit and additivity corrections (BACs). species related to this study include: Nitro-*n*-propane -29.8 kcal mol⁻¹, *n*-Propyl

nitrite $-27.9 \text{ kcal mol}^{-1}$, Nitro-*iso*-propane, $-33.6 \text{ kcal mol}^{-1}$ and Nitro-*tert*-butane: $-42.6 \text{ kcal mol}^{-1}$. Rice et al.³⁴ used a B3LYP/6-31G(d) based atomization energy calculations and atomic corrections to predict enthalpies of formation of several energetic materials: n-propyl nitrite $-28.1 \text{ kcal mol}^{-1}$, *tert*-nitrobutane $-41.50 \text{ kcal mol}^{-1}$, and *tert*-butyl nitrite $-36.7 \text{ kcal mol}^{-1}$, respectively. Osmont et al.³⁵ performed similar calculations at B3LYP/6-31G(d,p) level on nitro *n*-propane ($-33.10 \text{ kcal mol}^{-1}$), *iso*-nitropropane ($-35.90 \text{ kcal mol}^{-1}$) and *tert*-nitrobutane ($-43.20 \text{ kcal mol}^{-1}$), respectively. The heats of formation of n-propyl nitrite and *tert*-butyl nitrite obtained from isodesmic reactions at the B3P86/6-31G(d) level by Li et al.³⁶ are $-26.59 \text{ kcal mol}^{-1}$ and $-32.36 \text{ kcal mol}^{-1}$, respectively. In general, $\Delta_f H_{298}^0$ values are in good agreement with previous, evaluated literature (NIST) data, with the exception of *iso*-nitropropane which shows a several kcal mol^{-1} difference, where we suggest the new calculated value.

1.3 Computational Methods

The relative stability of RONO and RNO₂ isomers, homolytic bond dissociation energies and the heats of formation of radicals and molecules obtained from isodesmic reactions have been calculated using B3LYP hybrid density functional theory method in conjunction with the 6-31G(d,p) and 6-31+G(2d,2p) basis sets, as well the complete basis set-QB3 composite method. CBS-QB3 is a multilevel model chemistry that combines the results of several *ab initio* and DFT individual methods, and empirical terms to predict molecular energies with high accuracy and relatively low computational cost. The required electronic structure calculations are outlined as follows: (i) B3LYP/6-311G(2d,d,p) level geometry and frequencies; (ii) MP2/6-311G(3df,2df,2p) energy and

CBS extrapolation; (iii) MP4-(SDQ)/6-31G(d(f),p) energy; (iv) CCSD(T)/6-31+G(d') energy corrections. All quantum chemical calculations have been performed within the Gaussian-03 suite of programs.³⁷

To evaluate heats of formation of the titled systems we used variety of homodesmotic and isodesmotic work reactions, where the bonding environments are similar in products and reagents. A homodesmotic reaction is a hypothetical reaction where the number and type of bonds (hybridization of corresponding atoms) are conserved on both sides of the reaction. An isodesmotic reaction is one where the number of bonds of each type is conserved on each side of the work reaction.

1.4 Results and Discussion

1.4.1 Configuration of Nitrites

The optimized geometries at the CBS-QB3 composite level of theory, *viz.*, B3LYP/6-311(2d,d,p) calculations, for the target molecules and corresponding abbreviated nomenclature are presented in Figure 1.1

The torsional potentials of radicals (*vide infra*) show that corresponding *cis* and *trans*- isomers respective to the C-O-N-O dihedral angles have similar energies in the *n*-propyl and *iso*-propyl nitrites. The *tert*-butyl nitrite has a near 3 kcal mol⁻¹ lower energy for the *trans* configuration. The *cis* position of *n*-propyl nitrite has the terminal oxygen, which is equidistant from two hydrogen atoms at 2.516 Å, while the *cis* conformer of *iso*-propyl nitrite has the terminal oxygen atom at 2.28 Å distance from a hydrogen. The *cis* configuration in *n*-propyl nitrite is 0.36 kcal mol⁻¹ lower in energy than

corresponding *trans* configuration. For *iso*-propyl nitrite and *tert*-butyl nitrite, the *trans* configurations are 0.36 and 3.07 kcal mol⁻¹ lower than *cis* configurations, respectively.

1.4.2 Configuration of Nitro Alkanes

The oxygen atoms in the nitropropane are located at near gauche position (at 2.39 and 2.91 Å distances) relative to the H atoms on the adjacent carbon atoms. In 2-nitropropane one oxygen is eclipsed with the hydrogen atom on the central carbon atom. In 2-nitro-2-methyl propane one oxygen is eclipsed with a carbon atom. Structures are illustrated in Figure 1.1

1.4.3 Enthalpies of Formation

Enthalpies of formation ($\Delta_f H^\circ_{298}$) are evaluated using calculated electronic energies, zero point vibration energy corrections (ZPVE) and thermal contributions (to 298 K) for each of species in the work reaction.^{38, 3} Vibration frequencies are scaled by 0.9806 for CBS-QB3 level calculations.

Calculated reaction enthalpies, $\Delta_{\text{rxn}} H^\circ_{298}$, are used to find $\Delta_f H^\circ_{298}$ of the target molecules:

$$\Delta_{\text{rxn}} H^\circ_{298} = \sum H_f (\text{products}) - \sum H_f (\text{reactants}),$$

Where the two products and one reactant are the three reference molecules; we use the evaluated literature thermodynamic properties for the three reference species. The standard enthalpies of formation at 298.15 K for the reference species used in these reactions are summarized in Table 1.1

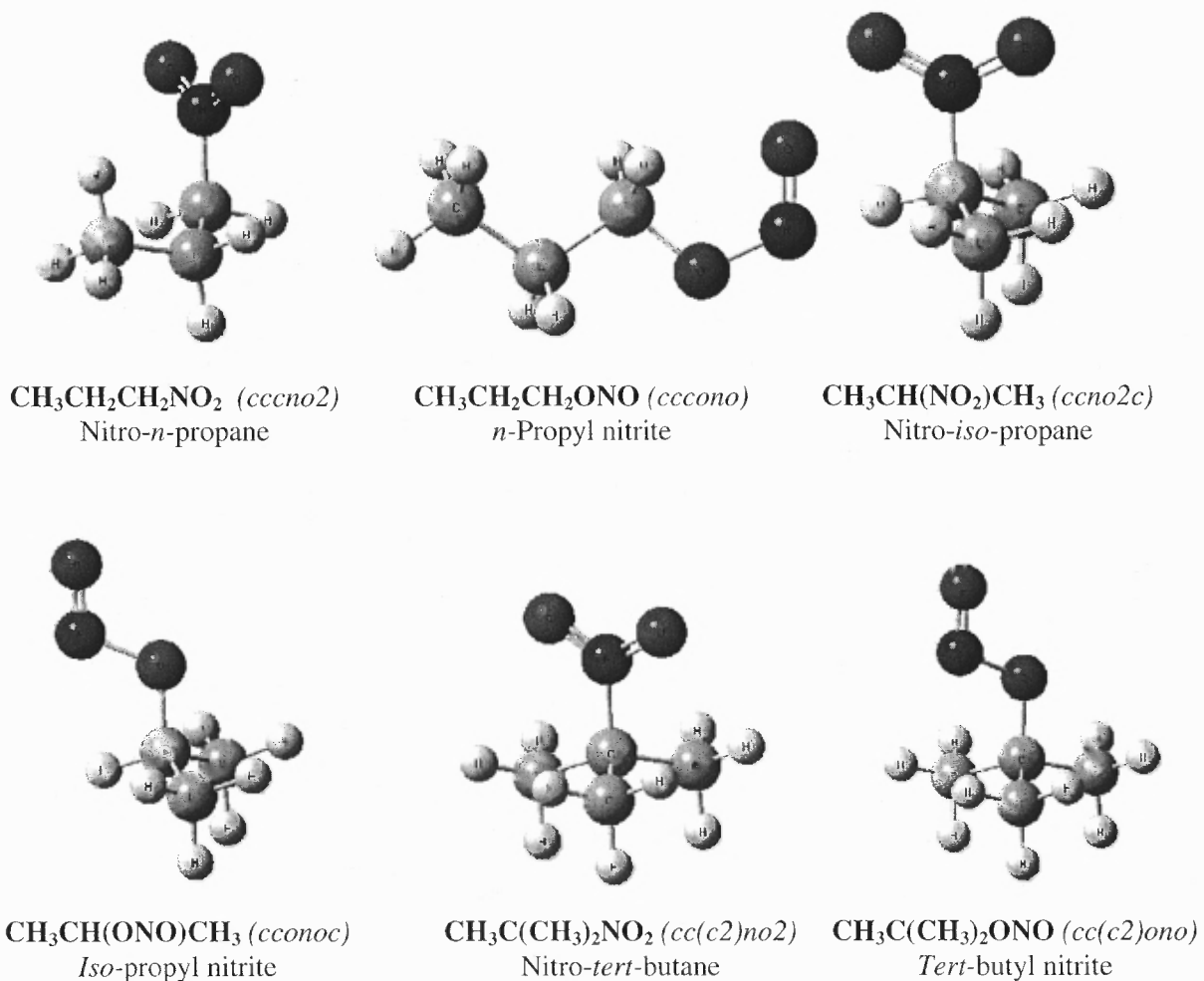
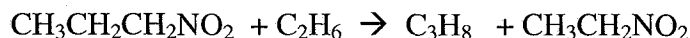


Figure 1.1 Geometry of the lowest energy conformers of the titled molecules and corresponding abbreviated nomenclatures (see appendix A, Table A1.1, for more details).

Table 1.1 Standard Enthalpies of Formation at 298.15 K of Reference Species used in work reactions for enthalpy of formation.

Species	$\Delta_f H^\circ_{298}$ kcal mol ⁻¹	Ref.
CH ₄	-17.89	39
C ₂ H ₆	-20.04	39
C ₂ H ₄	12.54	39
C ₃ H ₈	-25.02	39
C ₃ H ₆	4.88	39
CH ₃ CH ₂ CH ₂ CH ₃	-30.03	39
CH ₃ CH(CH ₃)CH ₃	-32.07	39
CH ₃ C(=O)CH ₃	-51.9	39
CH ₃ C(=O)H	-40.8	39
.CH ₃	34.82	39
C.H ₂ CH ₃	28.4	39
C.H ₂ CH ₂ CH ₃	23.9	39
CH ₃ C.HCH ₃	22	39
C.H ₂ CH(CH ₃)CH ₃	17	39
CH ₃ C.(CH ₃)CH ₃	11	39
CH ₃ C.HCH ₂ CH ₃	16	39
CH ₃ NO ₂	-17.67	3
CH ₃ ONO	-15.64	3
CH ₃ CH ₂ NO ₂	-25.06	3
CH ₃ CH ₂ ONO	-23.58	3
C.H ₂ NO ₂	31.53	3
C.H ₂ C(=O)CH ₃	-8.34	40
C.H ₂ C(=O)H	3.51	40

As an example, the following equation is used to estimate $\Delta_f H^\circ_{298}$ for CH₃CH₂CH₂NO₂



$\Delta_f H^\circ_{298}$ (kcal mol⁻¹): Target **-20.04** **-25.02** **-25.06**

Since enthalpies of formation of the three reference compounds (values above in bold) are well established in the literature. The heat of reaction, $\Delta_{\text{rxn}} H^\circ_{298}$, is calculated and the enthalpy of formation of the target molecule CH₃CH₂CH₂NO₂ is obtained as -30.64 kcal·mol⁻¹ from Hess's law.

The methods of isodesmic or homodesmic work reactions rely on the similarity of bonding environment in the reactants and products that leads to the cancellation of systematic errors in the ab initio and density functional theory calculations. The zero point energies are scaled by 0.9806 for B3LYP/6-31G(d,p) calculations as recommended by Scott et al⁴¹. The reaction enthalpies and the enthalpies of formation of the alkyl nitro and nitrites obtained from the use of the reaction schemes are shown in Table 1.2

In our previous studies,^{2,3} we calculated the thermochemistry of methyl and ethyl nitro and nitrite compounds and found that nitro alkanes are more stable than the corresponding nitrite isomers by ~ 8.0 kcal mol⁻¹ for HONO versus HNO₂, 2.03 kcal mol⁻¹ for CH₃NO₂ versus CH₃ONO, and 1.48 kcal mol⁻¹ for CH₃CH₂NO₂ versus CH₃CH₂ONO. Hence, the difference in $\Delta H_f^\circ_{298}$ between RNO₂ and RONO is expected to be about 1.7 kcal mol⁻¹. We do not observe a significant change in the RNO₂ vs RONO for primary vs. secondary vs. tertiary substituted nitro or nitrite compounds, where we thought a trend may occur due to differences in electronic properties. Comparisons of the calculated and evaluated experimental data show that the values computed at CBS-QB3 composite level, as it was expected are significantly closer to the experimental data; the agreement is excellent while comparing with NIST data base values (see Scheme 1).

Scheme 1. Formation enthalpies (kcal mol⁻¹) for a series of Nitro and Nitrite compounds calculated at CBS-QB3 level of theory in comparison with corresponding NIST data.

Species	This study	NIST reference
CH ₃ CH ₂ CH ₂ ONO	-28.4	-28.4
CH ₃ CH(ONO)CH ₃	-32.3	-31.9
CH ₃ C(CH ₃) ₂ NO ₂	-42.8	-42.3
CH ₃ C(CH ₃) ₂ ONO	-41.4	-41

We note that there are on average 3 kcal mol⁻¹ differences in B3LYP/6-31G(d,p) results between $\Delta_f H^0_{298}$ values evaluated in this study versus those calculated by Osmont et al.³⁵ Discrepancies are judged to result from differences in using isodesmic reaction analysis in our study, versus use of the optimized set of atomization conversion values derived from the calibration against seven selected RN_xO_y compounds in Osmont et al. work³⁵. Corresponding differences for *n*-nitropropane, *iso*-nitropropane and *tert*-nitrobutane are 3.1 kcal mol⁻¹, 3.3 kcal mol⁻¹ and 2.8 kcal mol⁻¹, respectively.

Table 1.2 Calculated Reaction Enthalpies at 298 K and Evaluated Enthalpies of Formation of Target Molecules^a
 (^a Reaction enthalpies include thermal correction and zero-point energy.)

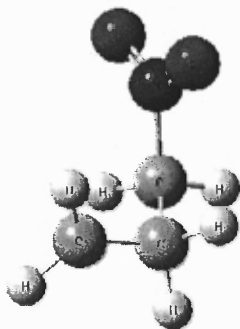
Work Reactions		$\Delta_f H^\circ(298)$ kcal mol ⁻¹					
		B3LYP		CBS-QB3			
		6-31G(d,p)	6-31+G(2d,2p)				
CH₃CH₂CH₂NO₂							
<i>cccno2</i>	+ C ₂ H ₆	--->	C ₃ H ₈	+ CH ₃ CH ₂ NO ₂	-30.09	-29.42	-30.64
<i>cccno2</i>	+ CH ₄	--->	C ₃ H ₈	+ CH ₃ NO ₂	-29.45	-29.24	-30.44
<i>cccno2</i>	+ C ₂ H ₄	--->	C ₃ H ₆	+ CH ₃ CH ₂ NO ₂	-30.32	-29.5	-30.61
Average					-29.96	-29.37	-30.57
CH₃CH₂CH₂ONO							
<i>cccono</i>	+ C ₂ H ₆	--->	C ₃ H ₈	+ CH ₃ CH ₂ ONO	-29.4	-28.35	-28.55
<i>cccono</i>	+ CH ₄	--->	C ₃ H ₈	+ CH ₃ ONO	-28.87	-28.46	-28.26
<i>cccono</i>	+ C ₂ H ₄	--->	C ₃ H ₆	+ CH ₃ CH ₂ ONO	-29.63	-28.43	-28.52
Average					-29.3	-28.42	-28.44
CH₃CH(NO₂)CH₃							
<i>cc(no2)c</i>	+ C ₂ H ₆	--->	C ₃ H ₈	+ CH ₃ CH ₂ NO ₂	-32.73	-32.43	-33.97
<i>cc(no2)c</i>	+ CH ₄	--->	C ₃ H ₈	+ CH ₃ NO ₂	-32.1	-32.25	-33.77
<i>cc(no2)c</i>	+ C ₂ H ₄	--->	C ₃ H ₆	+ CH ₃ CH ₂ NO ₂	-32.97	-32.51	-33.93
Average					-32.6	-32.4	-33.89

Table 1.2 (Continued)

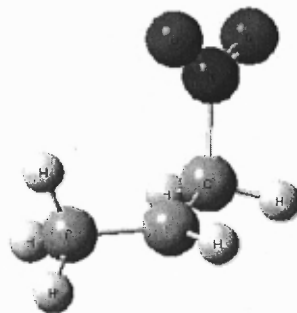
Work Reactions		$\Delta_f H^\circ(298)$ kcal mol ⁻¹					
		B3LYP			CBS-QB3		
		6-31G(d,p)	6-31+G(2d,2p)				
<i>cc(ono)c</i>	+ C ₂ H ₆	→	CH ₃ CH(ONO)CH ₃	+ C ₃ H ₈	-32.05	-32.41	-32.42
<i>cc(ono)c</i>	+ CH ₄	→	CH ₃ ONO	+ C ₃ H ₈	-31.52	-32.52	-32.14
<i>cc(ono)c</i>	+ C ₂ H ₄	→	CH ₃ CH ₂ ONO	+ C ₃ H ₆	-32.29	-32.49	-32.39
			Average		-31.95	-32.47	-32.32
<i>cc(c2)no2</i>	+ C ₂ H ₆	→	CH ₃ C(CH ₃) ₂ NO ₂	+ C ₃ H ₈	-40.91	-39.97	-42.83
<i>cc(c2)no2</i>	+ C ₃ H ₈	→	CH ₃ CH(CH ₃)CH ₃	+ C ₃ H ₈	-40.57	-39.93	-42.75
<i>cc(c2)no2</i>	+ C ₂ H ₆	→	CH ₃ CH ₂ CH ₂ NO ₂	+ C ₃ H ₈	-39.67	-39.19	-42.76
			Average		-40.38	-39.7	-42.78
<i>cc(c2)ono</i>	+ C ₂ H ₆	→	CH ₃ C(CH ₃) ₂ ONO	+ C ₃ H ₈	-39.44	-39.8	-41.43
<i>cc(c2)ono</i>	+ C ₃ H ₈	→	CH ₃ CH(ONO)CH ₃	+ C ₃ H ₈	-39.71	-39.7	-41.32
<i>cc(c2)ono</i>	+ C ₂ H ₆	→	CH ₃ CH ₂ CH ₂ ONO	+ C ₃ H ₈	-38.25	-39.11	-41.32
			Average		-39.13	-39.54	-41.36

Table 1.3 Formation Enthalpies for a Series of Nitro and Nitrite Compounds Calculated at Evaluated at Different Levels of Theory (Recommended Values are in **Bold**)

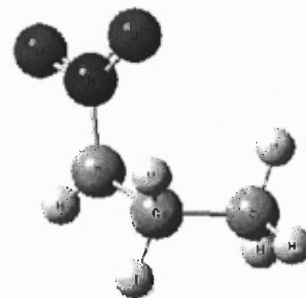
Species	$\Delta_f H^\circ(298)$ (kcal mol ⁻¹)		
	B3LYP/ 6-31+G(2d,2p)	CBS-QB3	Literature
CH ₃ CH ₂ CH ₂ NO ₂	-29.37	-30.57	-33.1 ³⁵ -29.8 ⁴⁹
CH₃CH₂CH₂ONO	-28.42	-28.44	-28.1 ³¹ -26.59 ³³ -27.9 ⁴⁹ -28.4 (NIST) ³⁹
CH ₃ CH(NO ₂)CH ₃	-32.4	-33.89	-35.9 ³⁵ -33.6 ⁴⁹
CH ₃ CH(ONO)CH ₃	-32.47	-32.32	-31.9 (NIST) ³⁹
CH ₃ C(CH ₃) ₂ NO ₂	-39.7	-42.78	-43.2 ³⁵ -41.5 ³¹ -42.6 ⁴⁹ -42.32 (NIST) ³⁹
CH ₃ C(CH ₃) ₂ ONO	-39.54	-41.36	-36.7 ³¹ -32.36 ³³ -41 (NIST) ³⁹



CH₂CH₂CH₂NO₂ (*cjccno2*)



CH₃CHCH₂NO₂ (*ccjcnno2*)



CH₃CH₂CHNO₂ (*cccjno2*)

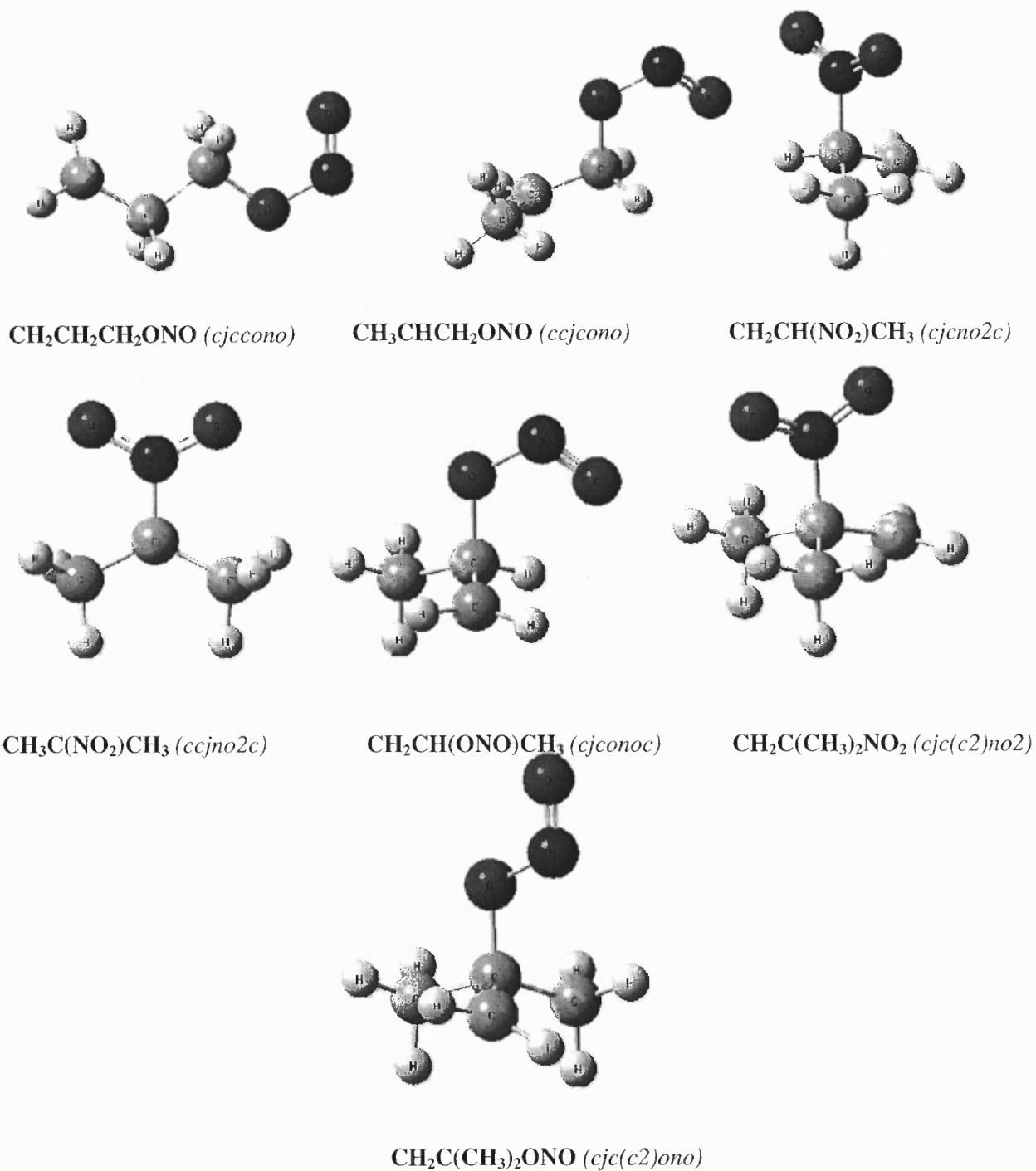


Figure 1.2 Illustrations of the lowest energy conformers of radicals corresponding to the loss of a hydrogen atom from parent molecules (see Table B1.2-B1.17, appendix B, for details) and nomenclature.

1.4.4 Bond Dissociation Energies

Bond energies are derived from $\Delta_f H^\circ_{298}$ of parent molecules and their radicals corresponding to the loss of hydrogen atoms. For the standard enthalpy of hydrogen atom at 298.15 K we used 52.103 kcal mol⁻¹. The resulted bond dissociation enthalpies computed from isodesmic enthalpies of formation are given in Table 1.4

We compare the bond energies against similar bond energies in alkanes.. We have used following values: primary 101.1 kcal mol⁻¹, secondary 98.5 kcal mol⁻¹ and tertiary 96.5 kcal mol⁻¹ for RC—H bond energies in alkanes. The C—H bonds on the carbon in alpha position to the NO₂/ONO groups show the largest deviation (decrease in bond energy of several kcal mol⁻¹). The bond energies for *cccjno2* and *ccj(no2)c* radical sites are 96 kcal mol⁻¹ and 92 kcal mol⁻¹ respectively. This is due to the resonance of the radical center with the electronegative NO₂ group. Kemnitz et al.⁴⁷ have reported a strong correlation between internal rotor barriers and resonance in C—N atoms for imides. We see a similar correlation on C—N bonded at nitro-carbon radical site.

The *cccjono* and *ccj(ono)c* radicals do not exist because the RO—NO bond at 43 kcal mol⁻¹ is much weaker than the carbonyl π -bond (~ 80 kcal mol⁻¹) formed in propanal CH₃CH₂C(=O)H and the acetone CH₃C(=O)CH₃ molecules, the potential products of the beta scission of corresponding RCjO—NO bonds. In effect, the radicals formed by loss of a hydrogen atom on the C—ONO bonded carbon, dissociate via *beta scission* to a carbonyl + NO immediately upon radical formation. Respective C—H bond energy in *cccjno2* (*n*-propyl nitrite) is estimated at 95 kcal mol⁻¹ from literature (transition state calculations).⁴⁸

The dissociation energies for primary methyl carbon—hydrogen bonds in nitro *n*-propane and *n*-propyl nitrite are the same as the primary RC—H bond energies in alkanes.

The primary carbon-hydrogen bond energies in nitro, and nitrite derivatives of *iso*-propane and *tert*-butane, are $102 \text{ kcal mol}^{-1}$, which is 1 kcal mol^{-1} higher than that in alkanes. These radical centers are located at beta positions to the electronegative NO_x group, separated by one sp^3 carbon bearing a partial positive charge. We interpret the increased bond energy as due to a polarization effect. C—H bonds of secondary carbon atoms in nitro-*n*-propane and *n*-propyl nitrite are $\sim 0.5 \text{ kcal mol}^{-1}$ stronger than respective bonds in alkanes ($\sim 99 \text{ kcal mol}^{-1}$); this also results through polarization from the adjacent (alpha position) carbon atom bonded to the ONO or NO_2 groups.

Table 1.4 Reaction Enthalpies at 298 K for Radicals, Calculated Enthalpies of Formation and Bond Energy^a

Work Reactions		Radicals Corresponding to H Atom Loss		$\Delta_f H^\circ(298)$ kcal mol ⁻¹				
				B3LYP		CBS-QB3		
				6-31G(d,p)	6-31+G(2d,2p)			
CH₃CH₂CH₂NO₂ system								
<i>cjccno2</i>								
<i>cjccno2</i>	+	CH ₃ CH ₂ CH ₃	→	<i>cccno2</i>	+ C.H ₂ CH ₂ CH ₃	19.19	19.84	18.79
<i>cjccno2</i>	+	CH ₃ CH ₃	→	<i>cccno2</i>	+ C.H ₂ CH ₃	19.39	20.33	19.01
<i>cjccno2</i>	+	CH ₄	→	<i>cccno2</i>	+ C.H ₃	18.9	19.92	19.59
				<i>Average</i>		19.16	20.03	19.13
				<i>Bond Energy H---CH₂CH₂CH₂NO₂</i>		101.22	101.52	101.8
CH₃CH₂CH₂ONO system								
<i>ccjcnno2</i>								
<i>ccjcnno2</i>	+	CH ₃ CH ₂ CH ₃	→	<i>cccno2</i>	+ CH ₃ C.HCH ₃	16.84	13.71	17.33
<i>ccjcnno2</i>	+	CH ₃ CH ₃	→	<i>cccno2</i>	+ C.H ₂ CH ₃	14.35	15.7	15.97
<i>ccjcnno2</i>	+	CH ₃ CH ₂ CH ₂ CH ₃	→	<i>cccno2</i>	+ CH ₃ C.HCH ₂ CH ₃	15.62	16.59	16.11
				<i>Average</i>		15.6	15.33	16.47
				<i>Bond Energy CH₃CH(---H)CH₂NO₂</i>		97.66	96.82	99.14
CH₃CH₂CH₂ONO system								
<i>cccjno2</i>								
<i>cccjno2</i>	+	CH ₃ CH ₂ CH ₃	→	<i>cccno2</i>	+ C.H ₂ CH ₂ CH ₃	10.64	12.32	12.72
<i>cccjno2</i>	+	CH ₃ CH ₃	→	<i>cccno2</i>	+ C.H ₂ CH ₃	10.84	12.81	12.94
<i>cccjno2</i>	+	CH ₃ NO ₂	→	<i>cccno2</i>	+ C.H ₂ NO ₂	13.04	13.98	14.1
				<i>Average</i>		11.51	13.04	13.25
				<i>Bond Energy CH₃CH₂CH(---H)NO₂</i>		93.56	94.53	95.92
CH₃CH₂CH₂ONO system								
<i>cjccono</i>								
<i>cjccono</i>	+	CH ₃ CH ₂ CH ₃	→	<i>cccno</i>	+ C.H ₂ CH ₂ CH ₃	19.46	20.31	20.4
<i>cjccono</i>	+	CH ₃ CH ₃	→	<i>cccno</i>	+ C.H ₂ CH ₃	19.66	20.8	20.62
<i>cjccono</i>	+	CH ₄	→	<i>cccno</i>	+ C.H ₃	19.17	20.39	21.21
				<i>Average</i>		19.43	20.5	20.74
				<i>Bond Energy H---CH₂CH₂CH₂ONO</i>		100.83	101.01	101.29

Table 1.4 (Continued)

Work Reactions			$\Delta_f H^\circ(298)$ kcal mol ⁻¹		CBS-QB3
			B3LYP		
			6-31G(d,p)	6-31+G(2d,2p)	
<i>ccjcono</i>	<i>cccono</i>	<i>cccono</i>	18.01	15.21	19.29
+ CH ₃ CH ₂ CH ₃	+ CH ₃ C.HCH ₃				
<i>ccjcono</i>	<i>cccono</i>	<i>cccono</i>	15.52	17.19	17.93
+ CH ₃ CH ₃	+ C.H ₂ CH ₃				
<i>ccjcono</i>	<i>cccono</i>	<i>cccono</i>	16.79	18.08	18.07
+ CH ₃ CH ₂ CH ₂ CH ₃	+ CH ₃ C.HCH ₂ CH ₃				
<i>Average</i>			16.77	16.83	18.43
<i>Bond Energy CH₃CH(---H)CH₂ONO</i>			98.17	97.34	98.97
CH₃CH(NO₂)CH₃ system					
<i>cjc(no2)c</i>	<i>cc(no2)c</i>	<i>cc(no2)c</i>	16.58	17.2	16.38
+ CH ₃ CH ₂ CH ₃	+ C.H ₂ CH ₂ CH ₃				
<i>cjc(no2)c</i>	<i>cc(no2)c</i>	<i>cc(no2)c</i>	16.78	17.69	16.6
+ CH ₃ CH ₃	+ C.H ₂ CH ₃				
<i>cjc(no2)c</i>	<i>cc(no2)c</i>	<i>cc(no2)c</i>	16.58	17.2	16.28
+ CH ₃ CH(CH ₃)CH ₃	+ C.H ₂ CH(CH ₃)CH ₃				
<i>Average</i>			16.65	17.36	16.42
<i>Bond Energy H---CH₂CH(NO₂)CH₃</i>			101.35	101.86	102.41
ccj(no2)c					
<i>ccj(no2)c</i>	<i>cc(no2)c</i>	<i>cc(no2)c</i>	5.7	2.64	7.32
+ CH ₃ CH ₂ CH ₃	+ CH ₃ C.HCH ₃				
<i>ccj(no2)c</i>	<i>cc(no2)c</i>	<i>cc(no2)c</i>	5.42	5.8	7.13
+ CH ₃ NO ₂	+ C.H ₂ NO ₂				
<i>ccj(no2)c</i>	<i>cc(no2)c</i>	<i>cc(no2)c</i>	4.86	5.36	5.11
+ CH ₃ CH(CH ₃)CH ₃	+ CH ₃ C.(CH ₃)CH ₃				
<i>Average</i>			5.33	4.6	6.52
<i>Bond Energy CH₃C(---H)(NO₂)CH₃</i>			90.02	89.1	92.51
CH₃CH(ONO)CH₃ system					
<i>cjc(ono)c</i>	<i>cc(ono)c</i>	<i>cc(ono)c</i>	16.94	18.15	17.62
+ CH ₃ CH ₂ CH ₃	+ C.H ₂ CH ₂ CH ₃				
<i>cjc(ono)c</i>	<i>cc(ono)c</i>	<i>cc(ono)c</i>	17.14	18.64	17.84
+ CH ₃ CH ₃	+ C.H ₂ CH ₃				
<i>cjc(ono)c</i>	<i>cc(ono)c</i>	<i>cc(ono)c</i>	16.95	18.15	17.51
+ CH ₃ CH(CH ₃)CH ₃	+ C.H ₂ CH(CH ₃)CH ₃				
<i>Average</i>			17.01	18.31	17.65
<i>Bond Energy H---CH₂CH(ONO)CH₃</i>			101.07	102.89	102.07

Table 1.4 (Continued)

Work Reactions		$\Delta_f H^\circ(298)$ kcal mol ⁻¹		CBS-QB3		
		B3LYP				
		6-31G(d,p)	6-31+G(2d,2p)			
CH₃C(CH₃)₂NO₂ system						
<i>cjc(c2)no2</i>						
<i>cjc(c2)no2</i>	+ CH ₃ CH ₂ CH ₃	---> <i>cc(c2)no2c</i>	+ C.H ₂ CH ₂ CH ₃	8.75	9.7	7.51
<i>cjc(c2)no2</i>	+ CH ₃ CH ₃	---> <i>cc(c2)no2c</i>	+ C.H ₂ CH ₃	8.95	10.19	7.73
<i>cjc(c2)no2</i>	+ CH ₃ CH(CH ₃)CH ₃	---> <i>cc(c2)no2c</i>	+ C.H ₂ CH(CH ₃)CH ₃	8.76	9.7	7.41
<i>Average</i>				8.82	9.86	7.55
<i>Bond Energy H---CH₂C(CH₃)₂NO₂</i>				101.3	101.66	102.43
CH₃C(CH₃)₂ONO system						
<i>cjc(c2)ono</i>						
<i>cjc(c2)ono</i>	+ CH ₃ CH ₂ CH ₃	---> <i>cc(c2)ono</i>	+ C.H ₂ CH ₂ CH ₃	10.11	9.97	8.55
<i>cjc(c2)ono</i>	+ CH ₃ CH ₃	---> <i>cc(c2)ono</i>	+ C.H ₂ CH ₃	10.31	10.46	8.76
<i>cjc(c2)ono</i>	+ CH ₃ CH(CH ₃)CH ₃	---> <i>cc(c2)ono</i>	+ C.H ₂ CH(CH ₃)CH ₃	10.12	9.97	8.44
<i>Average</i>				10.38	10.14	8.58
<i>Bond Energy H---CH₂C(CH₃)₂ONO</i>				101.41	101.77	102.05

^aReaction enthalpies include thermal correction and zero-point energy

Table 1.5 Summary of Formation Enthalpies ($\Delta_f H_{298}$) and Bond Dissociation Energies (BDE) for Nitroalkane and Alkyl Nitrite Molecules and their Carbon Radicals^a (in kcal mol⁻¹).

Molecules, Radicals and Selected Bonds	$\Delta_f H_{298}$ (in bold) and BDE (in <i>italic</i>)		
	B3LYP		CBS-QB3
	6-31G(d,p)	6-31+G(2d,2p)	
CH₃CH₂CH₂NO₂	-29.96	-29.37	-30.57
<i>cjccno2</i>	19.16	20.03	19.13
H---CH ₂ CH ₂ CH ₂ NO ₂	<i>101.22</i>	<i>101.52</i>	<i>101.8</i>
<i>ccjcnno2</i>	15.6	15.33	16.47
CH ₃ CH(---H)CH ₂ NO ₂	<i>97.66</i>	<i>96.82</i>	<i>99.14</i>
<i>cccjno2</i>	11.51	13.04	13.25
CH ₃ CH ₂ CH(---H)NO ₂	<i>93.56</i>	<i>94.53</i>	<i>95.92</i>
CH₃CH₂CH₂ONO	-29.3	-28.42	-28.44
<i>cjccono</i>	19.43	20.5	20.74
H--CH ₂ CH ₂ CH ₂ ONO	<i>100.83</i>	<i>101.01</i>	<i>101.29</i>
<i>ccjcono</i>	16.77	16.83	18.43
CH ₃ CH(---H)CH ₂ ONO	<i>98.17</i>	<i>97.34</i>	<i>98.97</i>
CH₃CH(NO₂)CH₃	-32.6	-32.4	-33.89
<i>cjc(no2)c</i>	16.65	17.36	16.42
H---CH ₂ CH(NO ₂)CH ₃	<i>101.35</i>	<i>101.86</i>	<i>102.41</i>
<i>ccj(no2)c</i>	5.33	4.6	6.52
CH ₃ C(---H)(NO ₂)CH ₃	<i>90.02</i>	<i>89.1</i>	<i>92.51</i>
CH₃CH(ONO)CH₃	-31.95	-32.47	-32.32
<i>cjc(ono)c</i>	17.01	18.31	17.65
H---CH ₂ CH(ONO)CH ₃	<i>101.07</i>	<i>102.89</i>	<i>102.07</i>
CH₃C(CH₃)₂NO₂	-40.38	-39.7	-42.78
<i>cjc(c2)no2</i>	8.82	9.86	7.55
H---CH ₂ C(CH ₃) ₂ NO ₂	<i>101.3</i>	<i>101.66</i>	<i>102.43</i>
CH₃C(CH₃)₂ONO	-39.13	-39.54	-41.36
<i>cjc(c2)ono</i>	10.18	10.14	8.58
H--CH ₂ C(CH ₃) ₂ ONO	<i>101.41</i>	<i>101.77</i>	<i>102.05</i>

^a Radicals are represented by abbreviated formulas, for simplicity; j represents a radical site.

1.4.5 Internal Rotation Potentials

Energy profiles for internal rotations about the C-C, C-O, C-NO₂, C—ONO and O-NO bonds in the nitroalkanes and alkyl nitrites were calculated to determine energies of the rotational conformers and interconversion barriers between isomers. Torsional potentials are then used to evaluate contributions to the entropy and heat capacity values from the low barrier (below 4.5 kcal mol⁻¹) rotors. The total energies as a function of the corresponding dihedral angles were computed at the B3LYP/6-31G(d,p) level of theory by scanning the torsion angles between 0° and 360° in steps of 15°, while all remaining coordinates were fully optimized. All potentials were re-scanned when a lower energy conformer, relative to the initial low energy conformer is found. The total energy of the corresponding most stable molecular conformer was arbitrarily set to zero and thus used as a reference point to plot the potential barriers. The resulting potential energy barriers for internal rotations in the stable non-radical and radical molecules are shown in Figs. 1.3.1–1.3.16 Dihedral angles obtained for the optimized lowest energy structures are shown in parenthesis.

The calculated rotational barriers of methyl groups in 1-nitropropane, 2-nitropropane and 2-nitro-2-methyl propane (Figs 1.3.1, 1.3.3 and 1.3.5) show the three-fold symmetry with the barriers of 3.0 kcal mol⁻¹, which is similar to the methyl rotor potentials in *n*-hydrocarbons. The C-NO₂ rotors in 1-nitro and 2-nitro propane exhibited low, 2-fold symmetric barriers of 1.25, and 0.6 kcal mol⁻¹ heights, respectively while the potential for 2-nitro-2-methyl propane had 6-fold symmetry with a barrier of 0.3 kcal mol⁻¹. RO--NO internal rotors all show symmetric 2-fold barriers of 12 to 14 kcal mol⁻¹ heights.

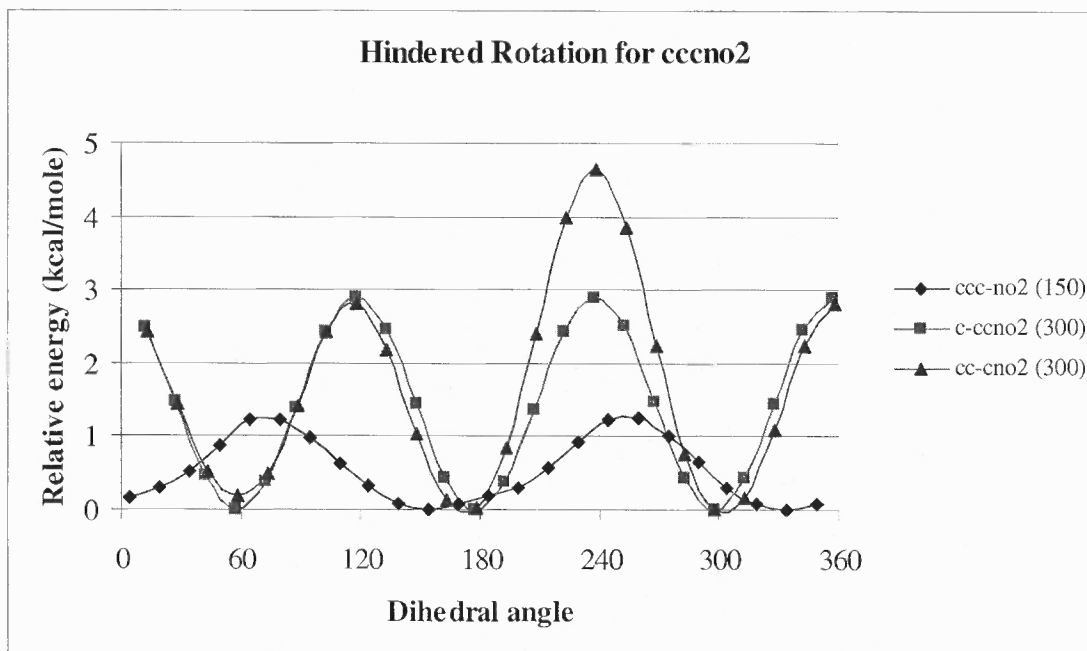


Figure 1.3.1 Potential Energy Profiles for Internal Rotations in Nitro-*n*-propane.

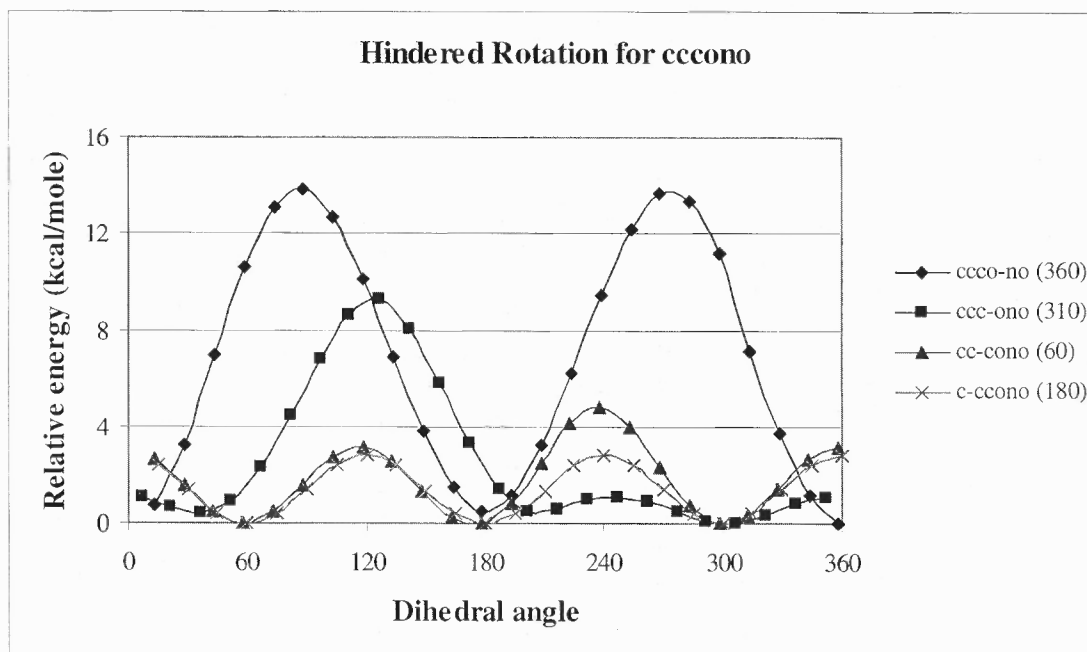


Figure 1.3.2 Potential Energy Profiles for Internal Rotations in *n*-propyl nitrite.

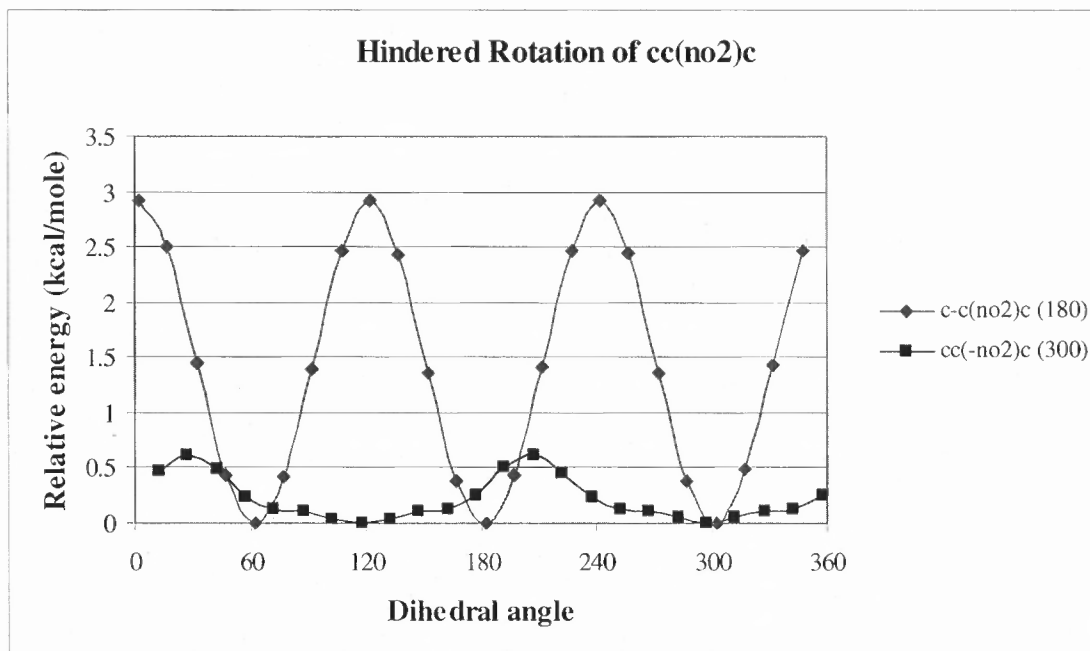


Figure 1.3.3 Potential Energy Profiles for Internal Rotations in Nitro-*iso*-propane.

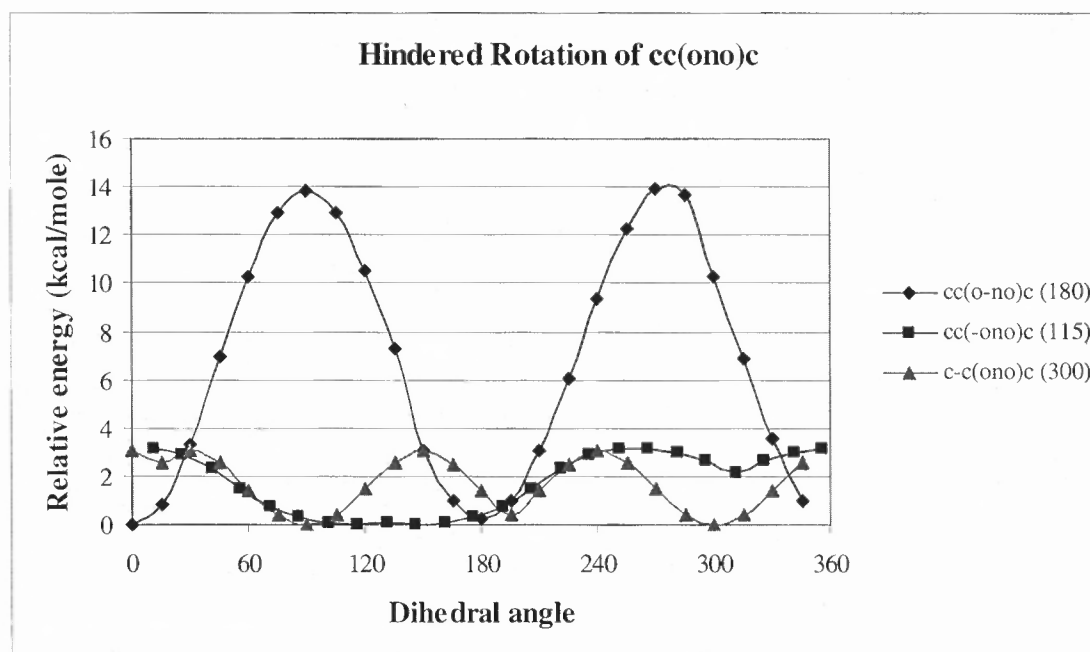


Figure 1.3.4 Potential Energy Profiles for Internal Rotations in *iso*-propyl nitrite

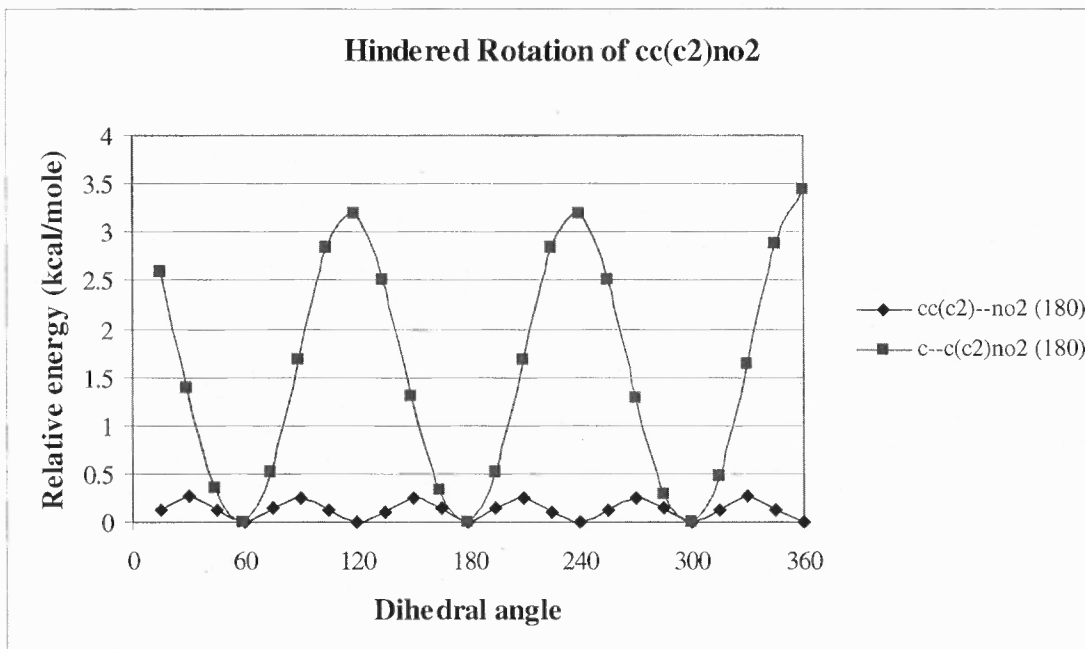


Figure 1.3.5 Potential Energy Profiles for Internal Rotations in Nitro-*tert*-butane

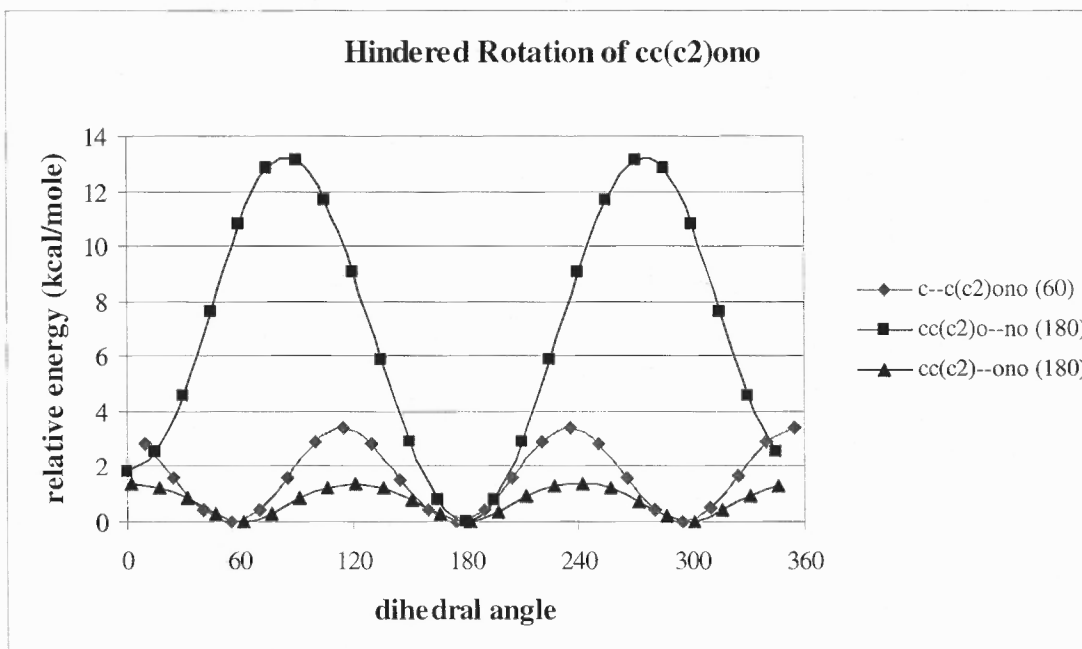


Figure 1.3.6 Potential Energy Profiles for Internal Rotations in *tert*-butyl nitrite

$\text{C}\cdot\text{H}_2\text{CH}_2\text{CH}_2\text{NO}_2$, γ -carbon radical of nitropropane, *cjccno2*.

The rotation barrier of the methyl group *cj--ccno₂* is reduced to $0.15 \text{ kcal mol}^{-1}$, nearly a free rotor, where the corresponding potential is six-fold and similar to that in a normal hydrocarbon. Instead, the *cjc--cno₂* rotor has a three-fold potential with one barrier located at 4.9 and two barriers at $2.6 \text{ kcal mol}^{-1}$. The *cjcc--no₂* rotor is similar to the non-radical nitropropane (parent molecule) with two-fold barriers at $1.25 \text{ kcal mol}^{-1}$.

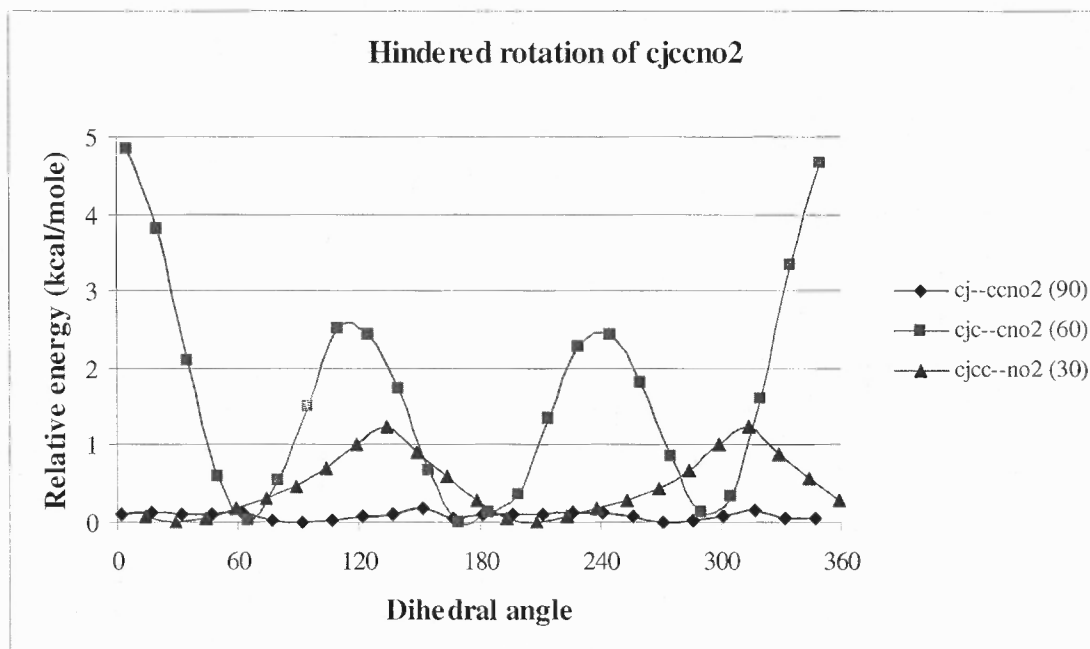


Figure 1.3.7 Potential Energy Profiles for Internal Rotations in $\text{C}\cdot\text{H}_2\text{CH}_2\text{CH}_2\text{NO}_2$ Radical (*cjccno2*)

$\text{CH}_3\text{C}\cdot\text{HCH}_2\text{NO}_2$, β -carbon radical of nitropropane, *ccjcn*o2

There are significant differences in all three internal rotor potentials in the *ccjcn*o2 (nitropropane -2yl) radical and the parent molecule. The *c--cjcno*2 methyl rotor is a three-fold one, but with extremely low barrier at $0.65 \text{ kcal mol}^{-1}$. For the *ccj--cno*2 rotor, there is a two-fold potential with barriers of 3.39 and $1.65 \text{ kcal mol}^{-1}$, respectively. The *ccjc--no*2 rotor has a four-fold potential with alternating 0.6 and $0.2 \text{ kcal mol}^{-1}$ barriers.

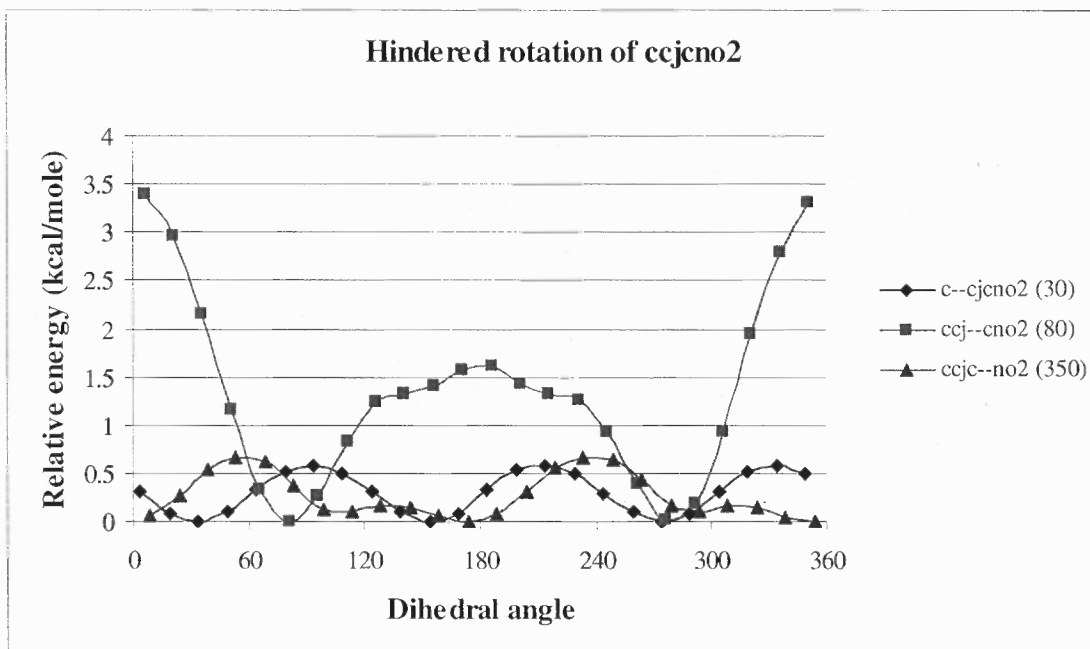


Figure 1.3.8 Potential Energy Profiles for Internal Rotations in $\text{CH}_3\text{C}\cdot\text{HCH}_2\text{NO}_2$ Radical (*ccjcn*o2)

$\text{CH}_3\text{CH}_2\dot{\text{C}}\cdot\text{HNO}_2$, α -carbon radical of nitropropane, *cccjno2*

The methyl rotor *c--ccjno2* is similar to a normal alkane as well as in the parent molecule. The potential foldness in the ethyl rotor *cc-cjno2* is similar to the parent molecule, but the barriers are reduced by near one half. The barrier for the $-\text{NO}_2$ rotor between nitrogen atom and the radical carbon site in *cccj--no2* is significantly high ($9.5 \text{ kcal mol}^{-1}$). The barrier increase ($8.25 \text{ kcal mol}^{-1}$) suggests a high degree of resonance between the carbon radical and the NO_2 group; this was also observed by Kemnitz et al.⁴⁷ (see also bond energy discussion above).

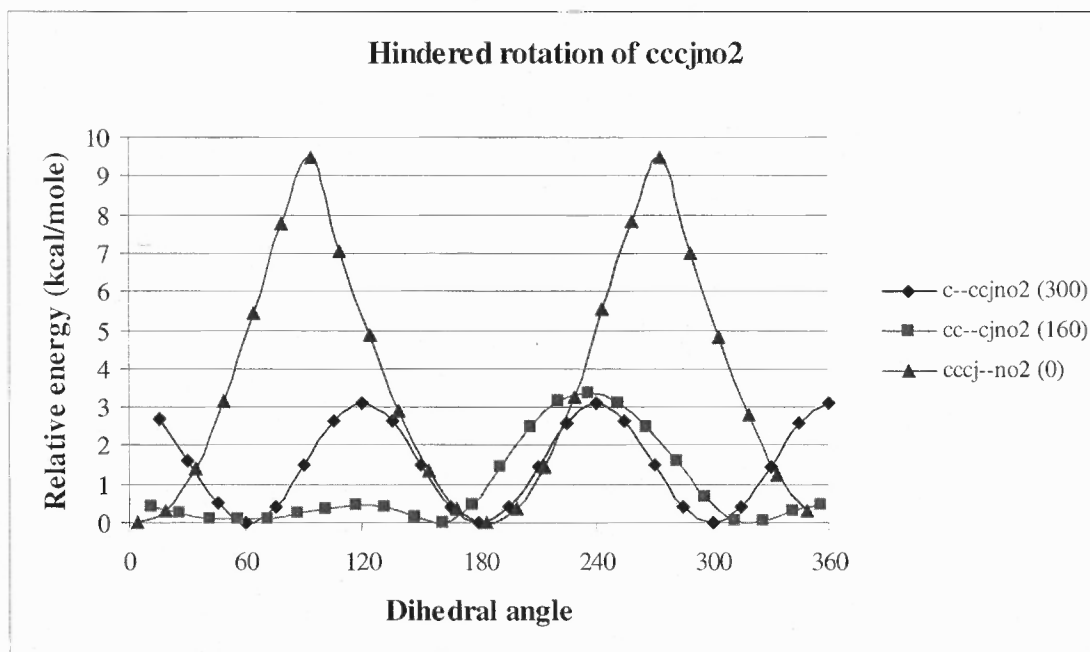


Figure 1.3.9 Potential energy profiles for internal rotations in $\text{CH}_3\text{CH}_2\dot{\text{C}}\cdot\text{HNO}_2$ Radical (*cccjno2*)

$C\cdot H_2CH_2CH_2ONO$, γ -carbon radical of propyl nitrite, *cjcono*

The *cjcono* the internal rotors are similar to those in the parent propyl nitrite, with the exception of the methyl rotor *cj--cono*, which has the barrier reduced from 3.0 to less than 0.5 kcal mol⁻¹. The 2-fold very high barrier (14.5 kcal mol⁻¹) in the *cjcco--no* rotor is similar to that in the parent molecule.

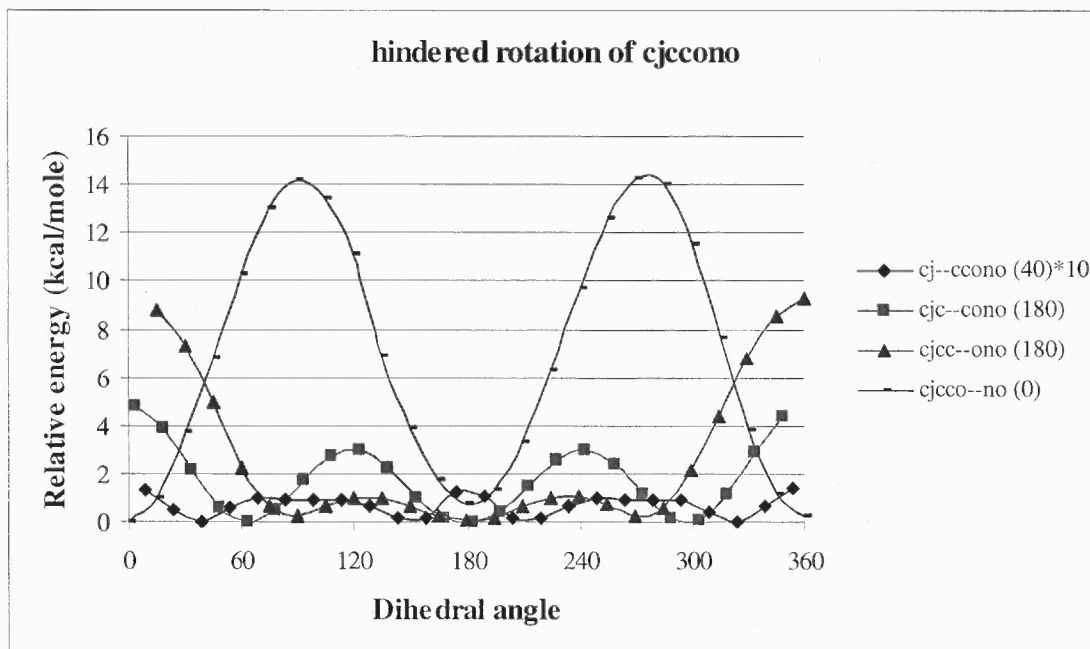


Figure 1.3.10 Potential Energy Profiles for Internal Rotation in $C\cdot H_2CH_2CH_2ONO$ Radical (*cjcono*)

CH₃C•HCH₂ONO, β -carbon radical of propyl nitrite, *ccjcono*

Barriers for the methyl and ethyl rotors in *ccjcono* are decreased relative to barriers in the parent molecule, and the *ccjc--ono* barrier is also decreased from 9.5 kcal mol⁻¹ in the parent to *ca* 6 kcal mol⁻¹ in this radical system. The two-fold *ccjco--no* rotor retains the high barrier (14.5 kcal mol⁻¹), which is similar to that in the parent molecule. The CH₃CH₂C•HONO radical (*cccjono*) is not stable; it undergoes rapid, exothermic dissociation to propanal plus NO upon formation of the carbon radical bonding to the ONO group. The alpha carbon radical immediately initiates formation of a strong π -bond (80 kcal mol⁻¹) in the carbonyl and cleaving the weak (43 kcal mol⁻¹) O—NO bond, as discussed above.

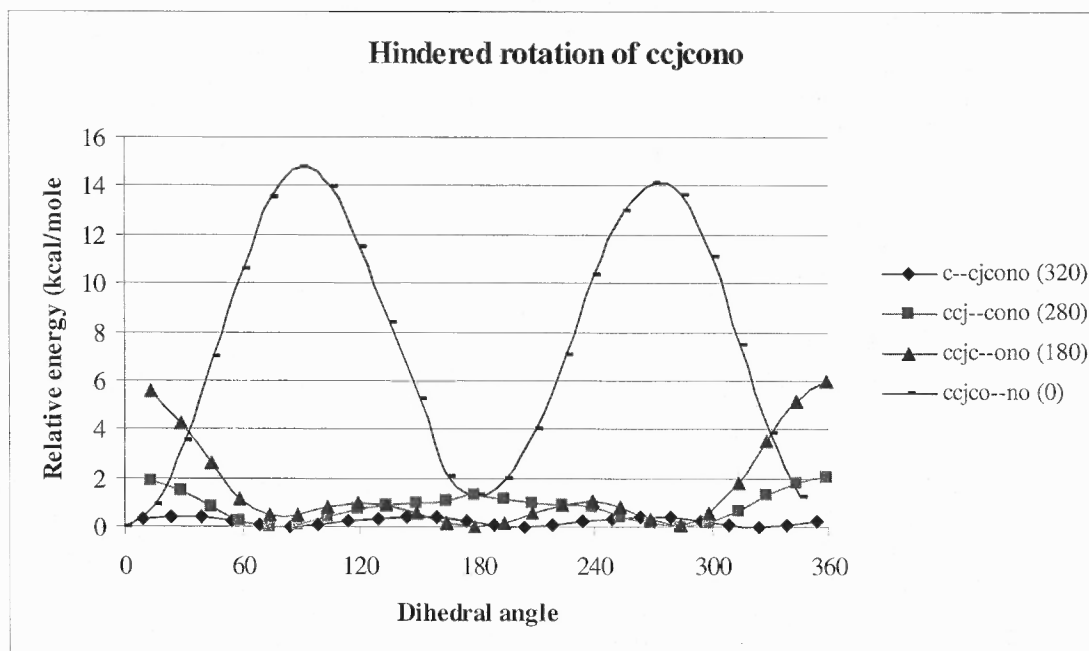


Figure 1.3.11 Potential Energy Profiles for Internal Rotation in CH₃C•HCH₂ONO Radical (*ccjcono*)

$\text{C}\cdot\text{H}_2\text{CH}_2(\text{NO}_2)\text{CH}_3$, primary carbon radical of nitro-iso-propane, *cjc(no2)c*.

The *cjc(--no2)c* rotor exhibits the same barriers as in the parent molecule with some distortion of the symmetric 2-fold potential of the parent, while the barrier of the methyl rotor is decreased from 3 to 1.4 kcal mol⁻¹

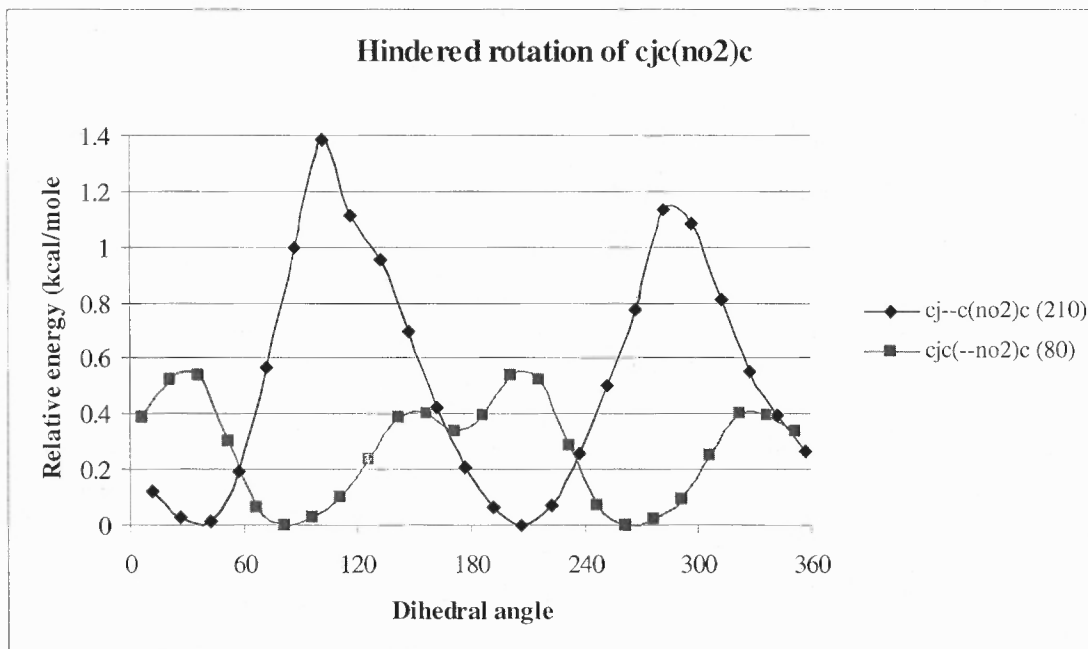


Figure 1.3.12 Potential Energy Profiles for Internal Rotation in $\text{C}\cdot\text{H}_2\text{CH}_2(\text{NO}_2)\text{CH}_3$ Radical (*cjc(no2)c*).

$\text{CH}_3\text{C}\cdot(\text{NO}_2)\text{CH}_3$, tertiary carbon radical of nitro-iso-propane, $\text{ccj}(\text{no}2)\text{c}$

The $c\text{-}cj(\text{no}2)\text{c}$ rotor is reduced to less than $0.1 \text{ kcal mol}^{-1}$, while the $\text{ccj}(\text{-no}2)\text{c}$ rotor is increased from 0.5 in 2 nitropropane to 11 kcal mol^{-1} in this radical, this is reflects in the 6 to 8 kcal mol^{-1} resonance, as determined from the decreased bond energy relative to a normal tertiary or secondary alkyl radical respectively, on this central carbon radical with the NO_2 group.

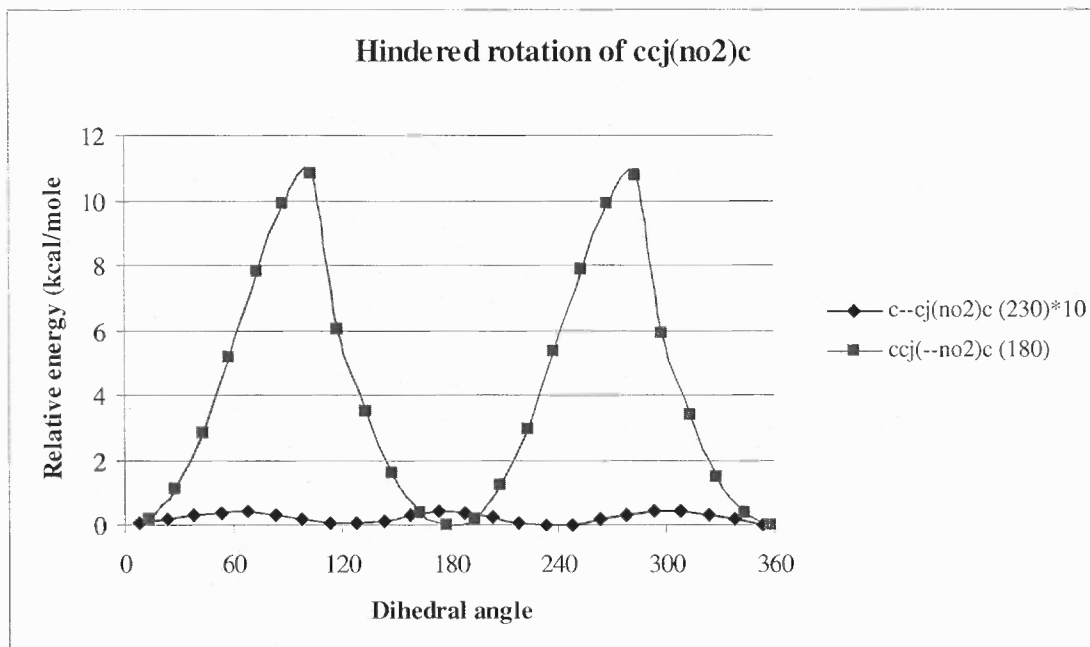


Figure 1.3.13 Potential Energy Profiles for Internal Rotation in $\text{CH}_3\text{C}\cdot\text{H}(\text{NO}_2)\text{CH}_3$ Radical ($\text{ccj}(\text{no}2)\text{c}$)

$\text{C}\cdot\text{H}_2\text{CH}_2(\text{ONO})\text{CH}_3$, primary carbon radical of iso-propyl nitrite, $\text{cjc}(\text{ono})\text{c}$

There are significant differences in two internal rotor potentials between $\text{cjc}(\text{ono})\text{c}$ radicals (*trans*- configurations) and the parent (*cis*-configuration). The $\text{cjc}(\text{--ono})\text{c}$ rotor has 3-folds with barrier of 9.1, 5.6 and 0.7 kcal mol⁻¹ while the methyl radical rotor barrier is decreased from 3 to 1.4 kcal mol⁻¹ and has a distorted two fold potential. The parent has a three fold potential. The $\text{cjc}(\text{c--no})\text{c}$ rotor is similar to that in the parent with a two fold potential and very high barrier (14 kcal mol⁻¹).

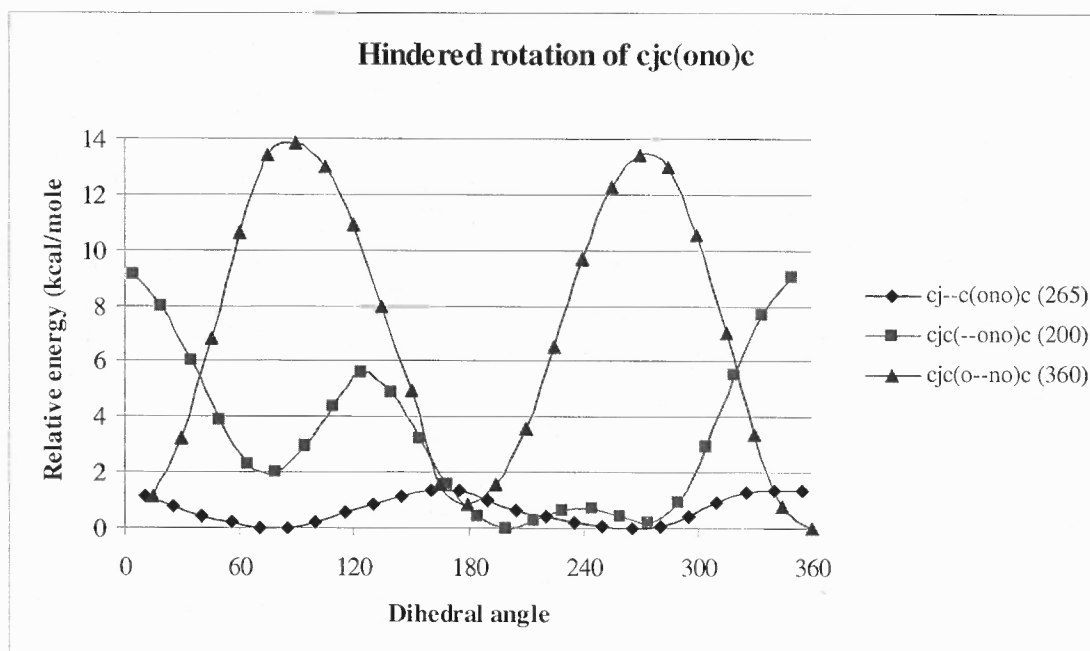


Figure 1.3.14 Potential Energy Profiles for Internal Rotation in $\text{C}\cdot\text{H}_2\text{CH}_2(\text{ONO})\text{CH}_3$ Radical ($\text{cjc}(\text{ono})\text{c}$)

$\text{C}\cdot\text{H}_2\text{CH}_2(\text{CH}_2)_2\text{NO}_2$, primary carbon radical of nitro-iso-butane, *cjc(c2)no2*

The NO_2 rotor in *cjc(c2)no2* shows a six fold barrier, four barriers at $0.28 \text{ kcal mol}^{-1}$ and two barriers at $0.12 \text{ kcal mol}^{-1}$. The $\text{CH}_2\cdot$ has an internal rotor barrier that is approximately one half that of the methyl in 2-nitro-2-methyl propane and is now a distorted two fold potential compared to three fold for the parent. The two methyl (CH_3 -) rotor profiles are similar to that of the CH_3 rotors on parent molecule and are not illustrated in Fig 1.3.15.

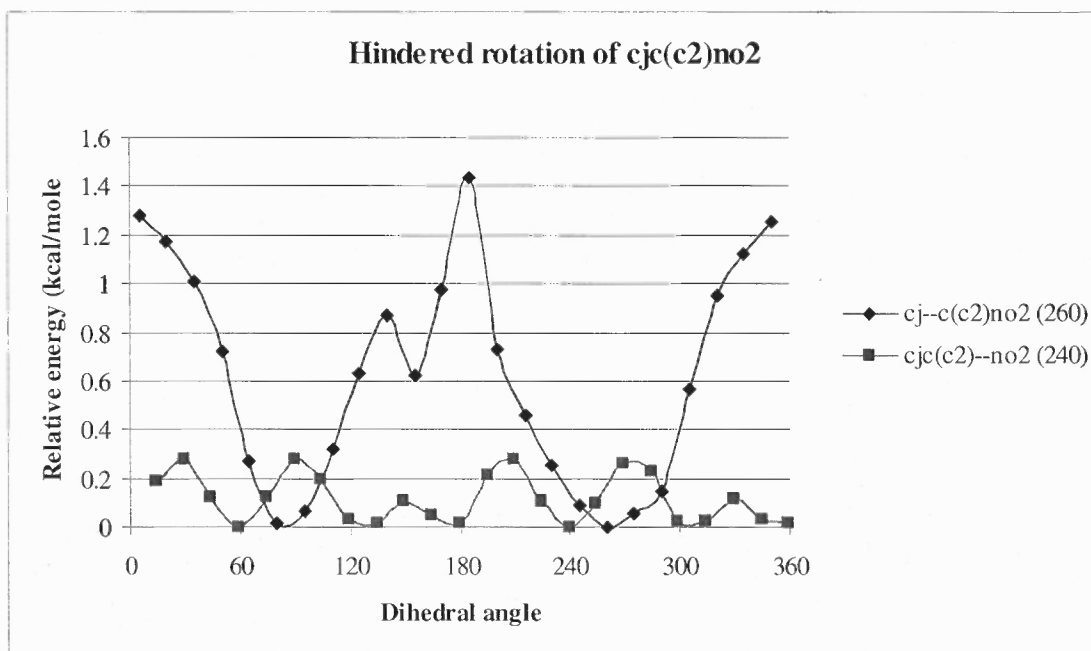


Figure 1.3.15 Potential Energy Profiles for Internal Rotation in $\text{C}\cdot\text{H}_2\text{CH}_2(\text{CH}_2)_2\text{NO}_2$ Radical (*cjc(c2)no2*)

$\text{C}\cdot\text{H}_2\text{CH}_2(\text{CH}_2)_2\text{ONO}$, primary carbon radical of *iso*-butyl nitrite, *cjc(c2)no2*

The methyl radical rotor has a two fold potential with barriers at $1.1 \text{ kcal mol}^{-1}$. The R--ONO rotor, *cjc(c2)--ono*, and the RO—NO rotor, *cj--c(c2)o-no*, are similar to the corresponding rotors in the closed-shell parents. The two methyl rotors are similar to those in the parent molecules and are not illustrated.

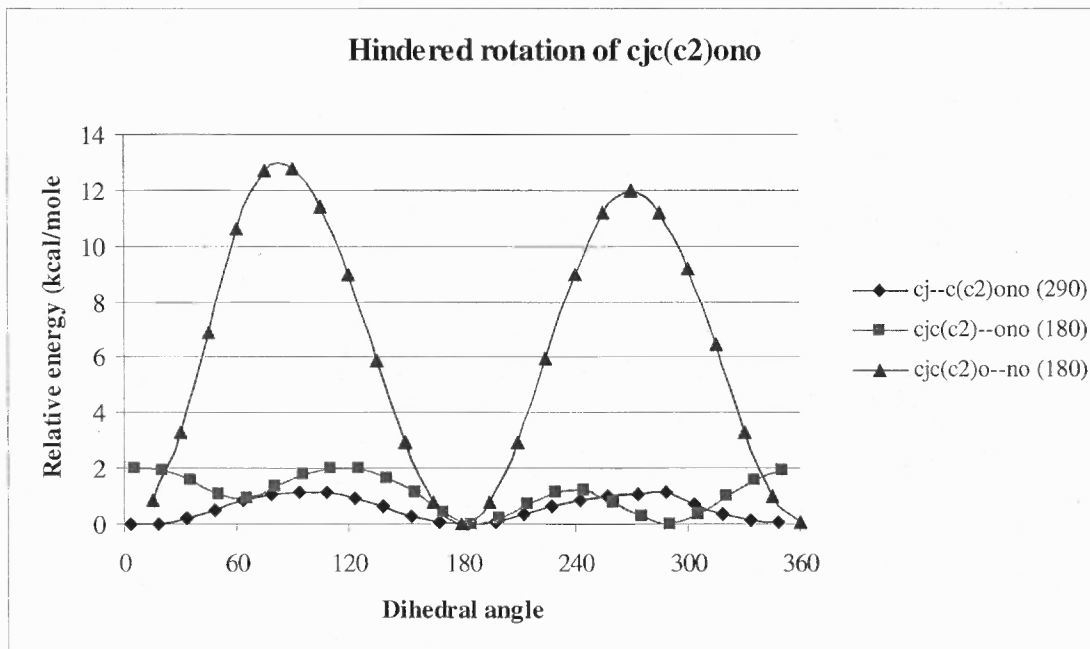


Figure 1.3.16 Potential Energy Profiles for Internal Rotation in $\text{C}\cdot\text{H}_2\text{CH}_2(\text{CH}_2)_2\text{ONO}$ Radical (*cjc(c2)ono*)

1.4.6 Entropy and Heat Capacity Data

Entropy and heat capacity contributions as a function of temperature are determined from the calculated structures, moments of inertia, vibration frequencies, symmetry, electron degeneracy, number of optical isomers and the known mass of each molecule. The calculations use standard formulas from statistical mechanics for the contributions of translation, external rotation and vibrations using the “SMCPS” program.⁴² This program utilizes the rigid-rotor-harmonic oscillator approximation from the frequencies along with

moments of inertia from the optimized CBS-QB3 structures, *viz.* B3LYP/6-311G(2d,d,p) level. Contributions from internal rotors (IR in Table 1.4) using Pitzer-Gwinn formalism^{45, 46} are substituted for contributions from internal rotor torsion frequencies where barriers were determined to be below 4.5 kcal mol⁻¹. These entropy and heat capacity data are needed to determine dependence of the enthalpy, entropy, Gibbs Energy and equilibrium constants with temperature. Entropy and heat capacity calculation were performed using complete basis set -QB3 determined geometries and harmonic frequencies summarized in Table 1.4

The entropy and heat capacity values of this study are compared with the recently published data of Ashcraft and Green⁴⁹ for the stable nitro alkane molecules and this is illustrated in Table Appendix A1.1 The values of entropy and heat capacity are all within in less than cal mol⁻¹ K⁻¹ with the exception of propane nitrite, which show some values of heat capacity varying by up to cal mol⁻¹ K⁻¹ and an entropy difference corresponding to $R \cdot \ln(3)$.

Table 1.6 Ideal Gas-phase Thermodynamic Property vs. Temperature

T(K)	CH ₃ CH ₂ CH ₂ NO ₂		CH ₃ CH ₂ CH ₂ ONO (<i>cis</i>)		CH ₃ CH(NO ₂)CH ₃	
	C _p (T)	S ⁰ (T) (6) ^b	C _p (T)	S ⁰ (T) (3)	C _p (T)	S ⁰ (T) (18)
5	7.95	29.95	7.95	31.48	7.95	27.63
50	7.98	48.26	8.46	49.90	8.04	45.95
100	8.87	53.99	10.91	56.46	9.54	51.89
150	10.65	57.90	13.49	61.37	11.71	56.15
200	12.93	61.26	15.96	65.58	14.03	59.83
250	15.59	64.42	18.63	69.42	16.62	63.23
298	18.42	85.50	21.42	84.93	19.34	82.77
300	24.72	67.51	25.49	73.07	24.99	66.50
350	21.62	70.59	24.55	76.60	22.42	69.71
400	30.57	73.67	31.18	80.07	30.77	72.89
500	35.80	79.78	36.39	86.80	35.93	79.13
600	40.24	85.74	40.84	93.24	40.30	85.17
700	44.13	91.46	44.43	99.36	44.15	90.95
800	47.13	96.93	47.83	105.15	47.12	96.45
900	50.05	102.12	50.20	110.63	50.05	101.66
1000	52.17	107.06	52.96	115.81	52.13	106.61
1200	56.20	116.20	56.06	125.37	56.26	115.77
1300	57.76	120.43	57.49	129.78	57.85	120.01
1400	59.15	124.47	58.73	133.98	59.28	124.05
1500	59.89	128.31	60.81	137.98	59.84	127.90
2000	60.53	145.16	62.64	155.44	60.54	144.75
2500	62.80	158.92	64.87	169.67	62.80	158.52
3000	64.15	170.50	66.20	181.62	64.15	170.09
3500	65.00	180.46	67.04	191.89	65.00	180.05
4000	65.58	189.17	67.60	200.88	65.58	188.77
4500	65.98	196.92	68.00	208.87	65.98	196.51
5000	66.27	203.89	68.28	216.04	66.27	203.48

Table 1.6 (Continued)

T(K)	CH ₃ CH(ONO)CH ₃ (<i>trans</i>)		CH ₃ C(CH ₃) ₂ NO ₂		CH ₃ C(CH ₃) ₂ ONO (<i>trans</i>)	
	C _p (T)	S ⁰ (T) (9)	C _p (T)	S ⁰ (T) (162)	C _p (T)	S ⁰ (T) (81)
5	7.95	29.36	7.95	24.51	7.95	26.20
50	8.15	47.70	8.03	42.82	8.11	44.53
100	10.15	53.87	10.01	48.84	10.61	50.75
150	12.76	58.48	13.26	53.50	14.27	55.74
200	15.34	62.50	16.61	57.76	17.85	60.32
250	18.02	66.21	20.08	61.83	21.43	64.68
298	20.73	85.13	23.58	86.25	24.94	89.68
300	27.49	69.74	31.11	65.80	33.38	68.90
350	23.73	73.17	27.43	69.73	28.75	73.04
400	33.20	76.53	38.69	73.62	40.45	77.10
500	38.06	83.04	45.20	81.27	46.47	85.01
600	42.10	89.25	50.57	88.67	51.50	92.59
700	45.39	95.15	55.00	95.76	55.94	99.79
800	48.40	100.73	58.83	102.49	59.37	106.62
900	50.70	106.02	62.00	108.89	62.77	113.08
1000	53.06	111.02	64.88	114.97	65.22	119.20
1200	56.15	120.25	69.24	126.22	70.04	130.52
1300	57.51	124.52	71.05	131.43	71.92	135.76
1400	58.70	128.58	72.64	136.40	73.61	140.74
1500	60.33	132.44	74.28	141.13	74.43	145.49
2000	60.67	149.35	74.61	161.88	74.74	166.29
2500	62.89	163.15	77.45	178.85	77.54	183.29
3000	64.21	174.74	79.15	193.13	79.21	197.58
3500	65.05	184.71	80.23	205.42	80.27	209.87
4000	65.61	193.43	80.95	216.18	80.99	220.64
4500	66.01	201.19	81.46	225.74	81.49	230.21
5000	66.30	208.16	81.83	234.35	81.85	238.81

Table 1.6 (Continued)

T(K)	<i>cjcno2</i>		<i>ccjno2</i>		<i>cccjno2</i>		<i>cjccono (cis)</i>		<i>ccjcono (trans)</i>	
	C _p (T)	S ⁰ (T)(4)	C _p (T)	S ⁰ (T)(6)	C _p (T)	S ⁰ (T)(3)	C _p (T)	S ⁰ (T)(2)	C _p (T)	S ⁰ (T)(3)
5	7.95	32.00	7.95	31.24	7.95	32.58	7.95	33.51	7.95	32.69
50	8.01	50.31	8.03	49.55	8.13	50.92	9.06	52.14	9.20	51.54
100	9.10	56.12	9.21	55.40	9.88	57.01	11.68	59.22	11.50	58.57
150	11.14	60.17	11.32	59.51	12.23	61.44	14.31	64.44	14.12	63.72
200	13.65	63.70	13.79	63.09	14.81	65.30	16.92	68.91	16.71	68.13
250	16.42	67.03	16.47	66.45	17.61	68.90	19.63	72.96	19.40	72.14
298	19.21	89.18	19.15	89.66	20.44	82.92	22.33	89.52	22.07	88.78
300	24.36	70.28	23.97	69.69	25.03	72.36	25.23	76.78	25.28	75.92
350	22.23	73.47	22.09	72.86	23.52	75.74	25.26	80.45	24.96	79.54
400	29.78	76.61	29.08	75.98	30.85	79.06	30.48	83.99	30.43	83.04
500	34.51	82.73	33.74	82.06	35.75	85.50	35.16	90.75	35.05	89.73
600	38.42	88.58	37.70	87.86	39.73	91.63	39.10	97.09	38.99	96.02
700	41.55	94.11	41.11	93.36	43.23	97.42	42.42	103.02	42.34	101.91
800	44.41	99.33	43.88	98.56	45.71	102.87	45.19	108.57	45.10	107.43
900	46.48	104.25	46.32	103.46	48.40	108.00	47.58	113.78	47.51	112.62
1000	48.73	108.89	48.38	108.09	49.99	112.83	49.60	118.67	49.54	117.49
1200	51.45	117.42	51.68	116.62	53.80	121.71	52.90	127.63	52.86	126.44
1300	52.67	121.36	53.01	120.56	55.19	125.80	54.23	131.75	54.20	130.55
1400	53.74	125.10	54.19	124.29	56.44	129.68	55.38	135.65	55.37	134.45
1500	55.36	128.65	55.22	127.85	56.52	133.37	56.33	139.36	56.32	138.15
2000	55.59	144.16	55.62	143.36	57.56	149.44	57.73	155.49	57.71	154.28
2500	57.52	156.78	57.55	156.00	59.50	162.51	59.61	168.59	59.61	167.38
3000	58.67	167.38	58.69	166.60	60.66	173.46	60.74	179.57	60.73	178.35
3500	59.40	176.48	59.42	175.70	61.39	182.87	61.45	188.99	61.45	187.77
4000	59.90	184.44	59.91	183.67	61.88	191.10	61.93	197.22	61.93	196.01
4500	60.24	191.52	60.25	190.74	62.23	198.41	62.27	204.54	62.27	203.32
5000	60.49	197.88	60.50	197.11	62.48	204.98	62.51	211.11	62.51	209.89

Table 1.6 (Continued)

T(K)	<i>cjc(no2)c</i>		<i>ccj(no2)c</i>		<i>cjc(ono)c (cis)</i>		<i>cjc(c2)no2</i>		<i>cjc(c2)ono (trans)</i>	
	C _p (T)	S ^o (T)(12)	C _p (T)	S ^o (T)(9)	C _p (T)	S ^o (T)(6)	C _p (T)	S ^o (T)(36)	C _p (T)	S ^o (T)(18)
5	7.95	31.09	7.95	30.29	7.95	31.16	7.95	28.80	7.95	31.28
50	8.06	49.41	9.06	49.05	8.10	49.48	8.08	47.12	8.18	49.62
100	9.67	55.39	11.08	55.91	10.03	55.57	10.34	53.25	10.91	55.98
150	12.12	59.76	13.44	60.84	12.82	60.15	13.85	58.09	14.80	61.12
200	14.74	63.60	15.90	65.03	15.66	64.22	17.42	62.56	18.60	65.89
250	17.48	67.17	18.51	68.85	18.52	68.02	20.98	66.82	22.28	70.43
298	20.18	87.46	21.15	83.84	21.26	81.19	24.41	92.07	25.74	94.93
300	25.39	70.60	23.25	72.46	24.74	71.64	31.56	70.95	34.36	74.80
350	23.08	73.93	24.04	75.94	24.16	75.14	28.06	74.99	29.36	79.05
400	30.53	77.18	28.75	79.32	30.07	78.53	38.34	78.95	40.99	83.17
500	35.03	83.45	33.72	85.83	34.59	85.01	44.10	86.62	46.35	91.09
600	38.78	89.39	37.93	91.99	38.30	91.10	48.82	93.90	50.69	98.55
700	41.80	94.97	41.45	97.79	41.42	96.79	52.86	100.78	54.45	105.55
800	44.58	100.22	44.41	103.25	43.98	102.12	56.09	107.27	57.35	112.13
900	46.60	105.17	46.93	108.39	46.24	107.12	59.10	113.38	60.21	118.31
1000	48.82	109.82	49.08	113.23	48.12	111.82	61.42	119.16	62.30	124.13
1200	51.48	118.38	52.51	122.13	51.26	120.43	65.66	129.80	66.35	134.84
1300	52.69	122.32	53.88	126.22	52.53	124.40	67.33	134.71	67.95	139.77
1400	53.74	126.06	55.07	130.11	53.65	128.16	68.83	139.38	69.39	144.46
1500	55.38	129.62	56.10	133.80	54.54	131.73	69.72	143.82	70.15	148.92
2000	55.60	145.13	57.63	149.90	55.73	147.29	69.66	163.23	69.78	168.37
2500	57.53	157.76	59.55	162.98	57.61	159.94	72.17	179.07	72.25	184.23
3000	58.68	168.36	60.70	173.94	58.73	170.55	73.67	192.36	73.73	197.54
3500	59.41	177.46	61.42	183.35	59.45	179.66	74.63	203.80	74.67	208.98
4000	59.90	185.43	61.91	191.59	59.93	187.63	75.27	213.80	75.30	218.99
4500	60.24	192.50	62.25	198.90	60.27	194.71	75.72	222.70	75.75	227.89
5000	60.49	198.86	62.50	205.47	60.52	201.07	76.05	230.69	76.07	235.89

^aThermodynamic properties are referred to standard state of an ideal gas at 1 atm. S^o(T) and C_p^o(T) are in cal mol⁻¹ K⁻¹

^bSymmetry numbers used for calculation of S^o(T) are in parenthesis

1.4.7 Group Values for use in the Group Additivity Method for Estimation of Thermochemical properties

Group additivity⁴³ is a straightforward and reasonably accurate calculation method to estimate thermodynamic properties of hydrocarbons and oxygenated hydrocarbons⁴⁴; it is particularly useful for application to larger molecules for use in codes or databases for the estimation of thermochemical properties in reaction mechanism generation. In this paper, we estimate six nitroalkanes, alkyl nitrites and the ten corresponding, carbon centered radical groups by using the thermodynamic property data developed in this study, plus the alkyl-hydrocarbon groups in the literature. The sixteen groups are listed in the Table 1.7, along with standard hydrocarbon groups used.

Comparison of group additivity data for three groups –with the data of Ashcraft and Green⁴⁹ (temperatures of 300 to 1500 K) are illustrated in Table Appendix A1.1 The Ashcraft and Green data are consistently a few tenths of a $\text{cal mol}^{-1} \text{K}^{-1}$ higher than the data in this study; we fee this is probably due to their treatment of all internal rotors as rotors, while we treat only rotors that have barriers below $4.5 \text{ kcal mol}^{-1}$

Table 1.7 Group Thermochemical Values Developed in this Study

Group	$\Delta_f H^\circ(298)$ (kcal mol ⁻¹)	$S^\circ(298)$ (cal mol ⁻¹ K ⁻¹)	$C_p^\circ(T)$ (cal mol ⁻¹ K ⁻¹)						
			300K	400K	500K	600K	800K	1000K	1500K
Groups developed in this study									
C/C/H2/NO2	-15.44	49.23	13.03	15.78	18.15	20.1	23.04	25.06	28.11
C/C/H2/ONO	-13.31	47.28	13.8	16.39	18.74	20.7	23.74	25.85	29.03
C/C2/H/NO2	-13.49	27.69	12.62	15.09	17.13	18.72	21.08	22.59	24.68
C/C2/H/ONO	-11.92	28.68	15.11	17.52	19.26	20.52	22.36	23.52	25.17
C/C3/NO2	-12.18	5.13	12.54	15.17	17	18.2	19.77	20.57	21.54
C/C3/ONO	-10.76	5	14.81	16.93	18.27	19.13	20.31	20.91	21.69
CJCCNO2	101.8	1.5	-0.36	-0.79	-1.29	-1.82	-2.72	-3.44	0
CCJCNO2	99.14	4.16	-0.75	-1.49	-2.06	-2.54	-3.25	-3.79	0
CCCJNO2	95.92	-3.96	0.31	0.28	-0.05	-0.51	-1.42	-2.17	0
CJCCONO	101.28	3.79	-0.26	-0.7	-1.23	-1.74	-2.64	-3.36	0
CCJCONO	98.97	3.05	-0.21	-0.75	-1.34	-1.85	-2.73	-3.42	0
CJCNO2C	102.41	3.89	-0.39	-0.24	-0.9	-1.52	-2.54	-3.31	0
CCJNO2C	92.51	-0.3	-1.75	-2.02	-2.21	-2.37	-2.71	-3.05	0
CJCONOC	102.07	-3.37	-2.75	-3.13	-3.47	-3.8	-4.42	-4.94	0
CJC2CNO2	102.43	2.83	0.45	-0.35	-1.1	-1.75	-2.74	-3.46	0
CJC2CONO	102.04	4.44	0.98	0.54	-0.12	-0.81	-2.02	-2.92	0
Known groups									
C/C/H3	-10.2	30.41	6.19	7.84	9.4	10.79	13.02	14.77	17.58
C/C2/H2	-4.93	9.42	5.5	6.95	8.25	9.35	11.07	12.34	14.2

^aSymmetry number (σ) is taken into account ($S = S_{\text{int}} - R \ln \sigma$)

1.5 Conclusions

Thermochemical properties, enthalpies of formation were observed to follow the trend of previous values of methyl and ethyl nitrate and nitro compounds. Our thermochemistry data $\Delta_f H^\circ_{298}$, $S^\circ(T)$ and $C_p^\circ(T)$ are in good agreement with data from Green et.al⁴⁹ calculated by CBS-QB3 with bond corrections. The enthalpies of formation of nitro alkanes were found to be slightly (*ca* ~ 1–2 kcal mol⁻¹) more stable (lower

enthalpy) than the corresponding nitrites, with the difference in $\Delta_f H^\circ_{298}$ between RNO_2 and $RONO$ remaining near constant at about $1.7 \text{ kcal mol}^{-1}$. Carbon -- hydrogen bond energies on the nitro-substituted carbon were observed to decrease by 2.5 to 8 kcal mol^{-1} relative to C-H bonds on corresponding alkanes. In contrast, the carbon - hydrogen bond energies were observed to increase by $\sim 1 \text{ kcal mol}^{-1}$ for carbon atoms located on beta position to the carbon bonded to the electronegative nitro / nitrite groups. C—H bonds on carbon atoms gamma to the nitro or nitrite group appeared to be identical to those on corresponding atoms in alkanes, within calculation error bar. Removal of a hydrogen atom from the carbon bonded to the nitrite (ONO) group resulted in exothermic reaction, with little or no barrier to form a carbonyl plus NO. Enthalpies of formation, entropy, $S^\circ(T)$ and heat capacity, $C_p^\circ(T)$, values are reported along with bond energies and corresponding thermochemical properties for 1 and 2 nitro -propane and 2-nitro 2-methyl propane and radicals corresponding to loss of hydrogen atom from the carbons sites. The computed enthalpies of formation via isodesmic work reactions and bond dissociation energies for nitroalkanes and alkyl nitrites are in satisfactory agreement with the limited experimental data available. Groups for use in group additivity are developed.

CHAPTER 2

THERMOCHEMICAL PROPERTIES FOR A SERIES OF NITROCARBONYLS, NITROOLEFINS

2.1 Overview

Structures, enthalpy ($\Delta_f H^\circ_{298}$), entropy (S°_{298}), and heat capacity ($C_p(T)$) are determined for a series of nitrocarbonyls, nitroolefins, corresponding nitrites and their carbon centered radicals using the density functional B3LYP and composite CBS-QB3 calculations. Enthalpies of formation ($\Delta_f H^\circ_{298}$) are determined at the B3LYP/6-31G(d,p), B3LYP /6-31+G(2d,2p) and composite CBS-QB3 levels using several work reactions for each species. Entropy (S) and heat capacity ($C_p(T)$) values from vibration, translational, and external rotational contributions are calculated using the rigid-rotor-harmonic-oscillator approximation based on the vibration frequencies and structures obtained from the density functional studies. Contribution to $\Delta_f H(T)$, S , and $C_p(T)$ from analysis on the internal rotors is included. Recommended values for enthalpies of formation of the most stable conformers of nitroacetone, 2 propane nitrite, nitroacetate and acetyl nitrite are -51.58 kcal mol⁻¹, -51.26 kcal mol⁻¹, -45.36 kcal mol⁻¹ and -58.17 kcal mol⁻¹, respectively. The calculated $\Delta_f H^\circ_{298}$ for nitroethylene is 7.59 kcal mol⁻¹ and for Vinyl nitrite is 7.23 kcal mol⁻¹.

2.2 Background Information

Accurate formation enthalpies, $\Delta_f H^\circ_{298}$, for nitro and nitrite molecules are required in order to understand reaction paths and assist in the development of detailed chemical kinetic mechanisms which can be applied to model the formation and destruction of nitrogen species in a variety of environments, particularly for atmospheric and combustion chemistries. Since less than 0.02% of known organic species have had their heats of formation measured¹ the application of quantum chemistry methods for this data is of value, provided that reasonable accuracy can be obtained. The establishment of these values will also aid in the determination of the thermochemical properties of higher homologues *via* use of isodesmic reactions with group conservation (isogeitonic reactions). This study continues development and evaluation of thermochemical properties on simplest nitro- and nitrite compounds from our previous analysis^{2,3}

Nitro (RNO_2) and nitrite ($RONO$) derivatives of hydrocarbons undergo thermal decomposition at relatively low temperatures and hence have potential as both propellants and energetic materials: the reaction barriers for bond cleavage of $R-NO_2$ (alkyl nitro compounds) and $RO-NO$ (corresponding nitrites) are *ca.* 61 and 40 kcal mol⁻¹, respectively.⁴⁻⁸ The nitro alkanes and alkyl nitrites can release NO and NO_2 and hence can serve as catalysts in oxidation of hydrocarbons.⁹⁻¹¹ In this regard, nitro compounds have been widely studied by both experimental and theoretical methods,^{4-8, 12-33} nevertheless, the thermochemical data are surprisingly limited.

The structures, heats of formation, bond dissociation energy, etc. of nitro and nitrite molecules have been the subject of many experimental and theoretical investigations. Shaw⁵⁰ used group additivity to predict $\Delta_f H^\circ_{298}$ in nitroethylene at 12.4

kcal mol⁻¹ and Dewar⁷ performed MINDO/3 calculation with 17.8 kcal mol⁻¹. Dixon¹² reported heat of formation by CCSD(T) calculation on energetic material with 9.5 kcal mol⁻¹ for nitroethylene while Benson⁵¹ also suggested 9 kcal mol⁻¹. Green et al.⁴⁹ perform thermochemical properties and group values for nitrogen-containing molecule with CBS-QB3 based atomization method with spin-orbit and additivity corrections (BACs): $\Delta_f H^\circ_{298}$ of vinyl nitrite and nitroethylene are 8.5 kcal mol⁻¹ and 8.9 kcal mol⁻¹, respectively.

In the present work, we have evaluated the formation enthalpies of several nitrocarbonyls, nitroolefins, corresponding nitrites and their carbon centered radicals based on their most stable rotation conformers using multilevel and individual computational chemistry methods. We used both complete basis set and Gaussian composite calculation methods. These methods employ a variety of different geometries, frequency determinations and higher order energy corrections (*vide infra*). The accuracy of these methods has been demonstrated in our previous studies on HONO isomers² and methyl and ethyl nitro and nitrite compounds.³

2.3 Computational Methods

The relative stability of RONO and RNO₂ isomers, homolytic bond dissociation energies and the heats of formation of radicals and molecules obtained from isodesmic reactions have been performed using B3LYP hybrid density functional theory method in conjunction with the 6-31G(d,p) and 6-31+G(2d,2p) basis sets, as well the complete basis set - QB3 composite method. CBS-QB3 is a multilevel model chemistry that combines the results of several *ab initio* and DFT individual methods and empirical terms to predict

molecular energies with high accuracy and relatively low computational cost. The required electronic structure calculations are outlined as follows: (i) B3LYP/6-311G(2d,d,p) level geometry and frequencies; (ii) MP2/6-311G(3df,2df,2p) energy and CBS extrapolation; (iii) MP4-(SDQ)/6-31G(d(f),p) energy; (iv) CCSD(T)/6-31G energy corrections. All quantum chemical calculations have been performed within the Gaussian-03 suite of programs.³⁴

We used variety of homodesmotic and isodesmotic work reactions, where the bonding environments are similar in products and reactants. A homodesmotic reaction is a hypothetical reaction where the number and type of bonds (according to the state of hybridization) are conserved on both sides of the reaction. An isodesmotic reaction is one where the number of bonds of each type, are conserved on each side of the work reaction.

2.4 Result and Discussion

The optimized geometries at the CBS-QB3 composite level of theory (*viz.*, B3LYP/6-311(2d,d,p) calculations) for the target molecules and corresponding abbreviated nomenclatures are presented in Figure 2.1 The *trans* configuration respective to C-O-N-O dihedral angles in 2 propane nitrite, vinyl nitrite and acetyl nitrite is more stable than corresponding *cis* isomer by 0.12 kcal mol⁻¹, 1.72 kcal mol⁻¹ and 3.94 kcal mol⁻¹, respectively. In nitroacetone and 2 propane nitrite, nitro and nitrite group are in *trans* configuration to carbonyl oxygen. One oxygen in nitroethylene and nitrogen in vinyl nitrite is eclipsed with hydrogen atom on the first carbon while one oxygen in nitroacetate and nitrogen in acetyl nitrite is eclipsed with carbonyl oxygen.

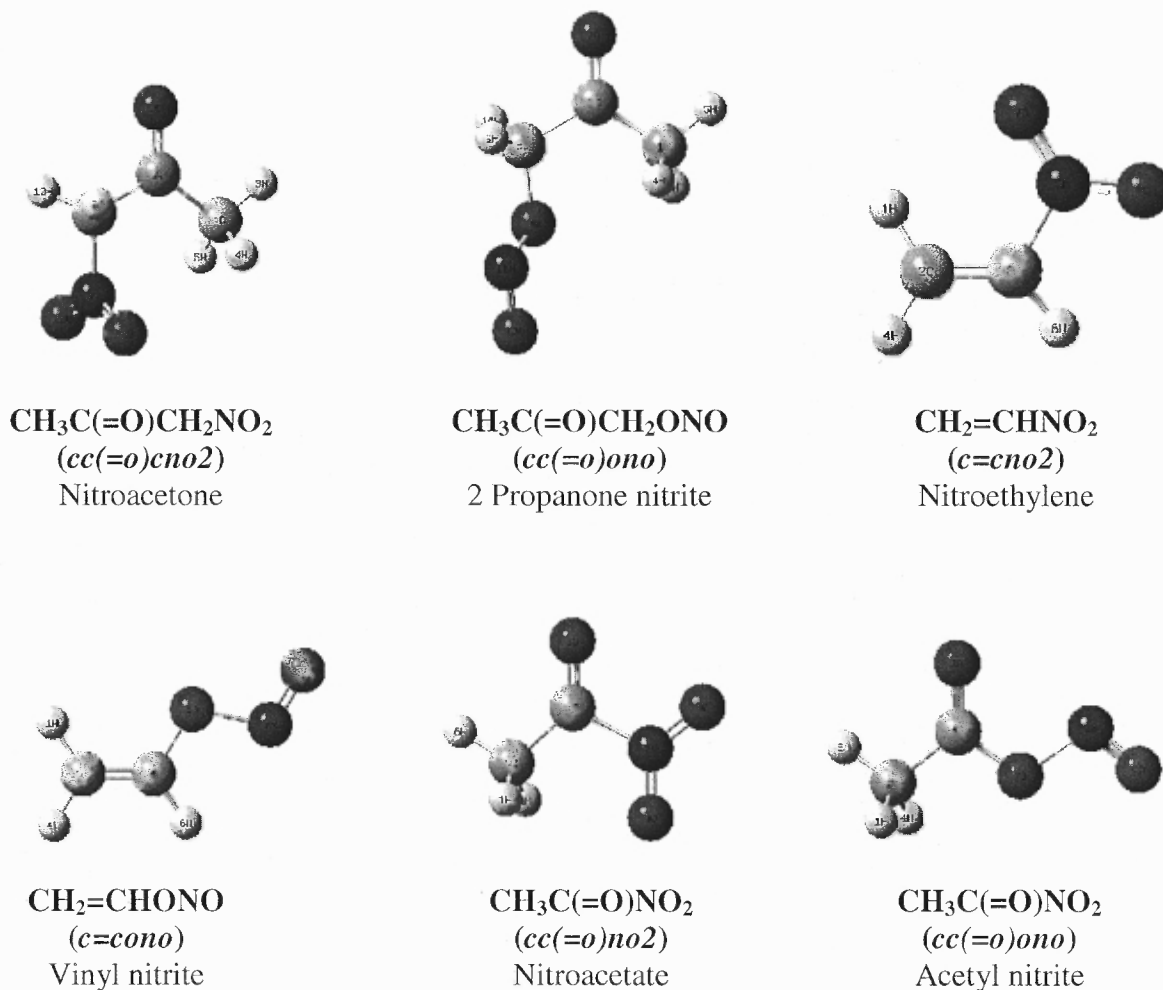


Figure 2.1 Geometry of the lowest energy conformer of the target molecules and abbreviated nomenclatures (see appendix C, Table C2.2-C2.15 for more details).

2.4.1 Enthalpies of Formation

Energies from the CBS-QB3 composite level are used with a series of isodesmic reactions having bond conservation to estimate the enthalpy of formation ($\Delta_f H^\circ_{298}$) for target molecules. The total energies are corrected by zero-point vibration energies (ZPVE), which are scaled by 0.97 as recommended by Scott and Radom.⁴¹ Thermal correction, 0-298.15 K, is calculated to estimate $\Delta_f H^\circ_{298}$ at 298.15 K. We use the calculated $\Delta_{\text{rxn}} H^\circ_{298}$ in the formula to find $\Delta_f H^\circ_{298}$ of the target reactant:

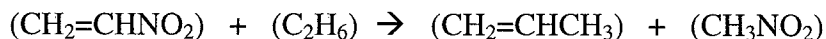
$$\Delta_{\text{rxn}}H^{\circ}_{298} = \sum H_f \text{ products} - \sum H_f \text{ reactants}$$

Where the two products and one reactant are the three reference molecules, we use the evaluated literature thermodynamic properties for the three reference species. The standard enthalpies of formation at 298.15 K of the reference species used in these reactions are summarized in Table 2.1

Table 2.1 The Standard Enthalpies of Formation at 298.15 K of Reference Species

Species	$\Delta_f H^{\circ}_{298}$ (kcal mol ⁻¹)	Source (Ref. No.)
CH ₄	-17.89	39
C ₂ H ₄	12.54	39
C ₂ H ₆	-20.04	39
C ₃ H ₈	-25.02	39
C ₃ H ₆	4.88	39
CH ₂ =CHCH ₂ CH ₃	-0.15	39
C.H=CH ₂	71	39
CH ₃ C.HCH ₃	22	39
C.H ₂ CH ₂ CH ₃	23.9	39
CH ₃ C(=O)CH ₃	-51.9	39
CH ₂ =CH.CH ₂	39.13	52
C.H=CHCH ₃	64.3	52
CH ₂ =C.CH ₃	58.89	52
CH ₃ NO ₂	-17.67	2
CH ₃ ONO	-15.64	2
CH ₃ CH ₂ NO ₂	-25.06	2
CH ₃ CH ₂ ONO	-23.58	2
C.H ₂ NO ₂	31.53	2
C.H ₂ C(=O)CH ₃	-8.34	53
C.H ₂ C(=O)H	3.51	53
CH ₃ C(=O)H	-39.7	53

As an example, the following equation is used to estimate $\Delta_f H^\circ_{298}$ for $\text{CH}_2=\text{CHNO}_2$



$\Delta_f H^\circ_{298}$ (kcal mol⁻¹): **Target** **-20.04** **4.88** **-17.67**

Since enthalpies of formation of the three reference compounds (in bold above) are well established in the literature, the $\Delta_{\text{rxn}} H^\circ_{298}$ is calculated and the enthalpy of formation of the target molecule $\text{CH}_2=\text{CHNO}_2$ is obtained from Hess's law.

The method of isodesmic reactions utilizes a similarity in the bonding environments for reactant and product sets in a work reaction to effect a cancellation of systematic errors in the *ab initio* or density functional calculations. The basic requirement of an isodesmic reaction is that the number of each type of bond is conserved in the reaction. The zero point energies are scaled by 0.9806, as recommended by Scott et al⁴¹ for B3LYP/6-31G(d,p) and thermal correction to 298.15K. Calculations are performed on each species in three work reactions for each molecule. The reaction enthalpies and the enthalpies of formation of the target molecules obtained from the use of the reaction schemes are shown in Table 2.2

Table 2.2 Calculated Reaction Enthalpies at 298 K and Evaluated Enthalpies of Formation of Target Molecules^a

Work Reactions		$\Delta H^\circ(298)$ kcal mol ⁻¹					
		B3LYP		CBS-QB3			
		6-31G(d,p)	6-31+G(2d,2p)				
CH₃C(=O)CH₂NO₂							
<i>cc(=o)cno2</i>	+ C ₂ H ₆	→	CH ₃ C(=O)CH ₃	+ CH ₃ CH ₂ NO ₂	-51.94	-51.13	-51.71
<i>cc(=o)cno2</i>	+ CH ₄	→	CH ₃ C(=O)CH ₃	+ CH ₃ NO ₂	-51.3	-50.95	-51.51
<i>cc(=o)cno2</i>	+ C ₃ H ₆	→	CH ₃ C(=O)CH ₃	+ CH ₂ =CHCH ₂ NO ₂	-50.29	-50.49	-51.52
			Average		-51.18	-50.86	-51.58
CH₃C(=O)CH₂ONO							
<i>cc(=o)cono</i>	+ C ₂ H ₆	→	CH ₃ C(=O)CH ₃	+ CH ₃ CH ₂ ONO	-52.51	-51.74	-51.24
<i>cc(=o)cono</i>	+ CH ₄	→	CH ₃ C(=O)CH ₃	+ CH ₃ ONO	-51.98	-51.84	-50.96
<i>cc(=o)cono</i>	+ C ₃ H ₆	→	CH ₃ C(=O)CH ₃	+ CH ₂ =CHCH ₂ ONO	-51.18	-50.86	-51.57
			Average		-51.89	-51.48	-51.26
CH₂=CHNO₂							
<i>c=cno2</i>	+ C ₂ H ₆	→	CH ₂ =CHCH ₃	+ CH ₃ NO ₂	6.29	6.88	7.69
<i>c=cno2</i>	+ C ₃ H ₈	→	CH ₂ =CHCH ₂ CH ₃	+ CH ₃ NO ₂	5.89	7.48	7.42
<i>c=cno2</i>	+ C ₃ H ₈	→	CH ₂ =CHCH ₃	+ CH ₃ CH ₂ NO ₂	6.86	7.08	7.66
			Average		6.34	7.17	7.59

Table 2.2 (continued)

Work Reactions		$\Delta H^\circ(298)$ kcal mol ⁻¹					
		B3LYP					
		6-31G(d,p)	6-31+G(2d,2p)	CBS-QB3			
CH₂=CHONO							
<i>c=cono</i>	+ C ₂ H ₆	--->	CH ₂ =CHCH ₃	+ CH ₃ ONO	6.3	4.74	7.38
<i>c=cono</i>	+ C ₃ H ₈	--->	CH ₂ =CHCH ₂ CH ₃	+ CH ₃ ONO	5.9	5.34	7.1
<i>c=cono</i>	+ C ₃ H ₈	--->	CH ₂ =CHCH ₃	+ CH ₃ CH ₂ ONO	6.4	4.82	7.23
			Average		6.2	4.97	7.23
CH₃C(=O)NO₂							
<i>cc(=o)no2</i>	+ C ₂ H ₆	--->	CH ₃ C(=O)CH ₃	+ CH ₃ NO ₂	-47.83	-45.26	-45.32
<i>cc(=o)no2</i>	+ C ₃ H ₆	--->	CH ₃ C(=O)CH ₃	+ CH ₂ =CHNO ₂	-46.53	-44.55	-45.42
<i>cc(=o)no2</i>	+ C ₃ H ₈	--->	CH ₃ C(=O)CH ₃	+ CH ₃ CH ₂ NO ₂	-47.26	-45.06	-45.35
			Average		-47.21	-44.96	-45.36
CH₃C(=O)ONO							
<i>cc(=o)ono</i>	+ C ₂ H ₆	--->	CH ₃ C(=O)CH ₃	+ CH ₃ ONO	-58.71	-58.15	-58.08
<i>cc(=o)ono</i>	+ C ₃ H ₆	--->	CH ₃ C(=O)CH ₃	+ CH ₂ =CHONO	-57.78	-55.66	-58.22
<i>cc(=o)ono</i>	+ C ₃ H ₈	--->	CH ₃ C(=O)CH ₃	+ CH ₃ CH ₂ ONO	-58.6	-58.07	-58.22
			Average		-58.36	-57.29	-58.17

Table 2.3 Formation Enthalpies for a Series of Nitrocarbonyls, Nitroolefins Compounds Calculated at Evaluated at Different Levels of Theory (Recommended Values are in Bold)

Species	$\Delta_f H^\circ(298)$ kcal mol ⁻¹		
	B3LYP		CBS-QB3
	6-31G(d,p)	6-31+G(2d,2p)	
CH ₃ C(=O)CH ₂ NO ₂	-51.18	-50.86	-51.58
CH ₃ C(=O)CH ₂ ONO	-51.89	-51.48	-51.26
CH ₂ =CHNO ₂	6.34	7.17	7.59
CH ₂ =CHONO	6.2	4.97	7.23
CH ₃ C(=O)NO ₂	-47.21	-44.96	-45.36
CH ₃ C(=O)ONO	-58.36	-57.29	-58.17

Lowest energy configuration structures of the radicals are illustrated in Figure 2.2

2.4.2 Bond Dissociation Energies

Bond energies are reported from the calculated the $\Delta_f H^\circ_{298}$ of the parent molecule and its radical corresponding to loss of hydrogen atoms, where the enthalpies of parent molecule and product species are calculated in this study in conjunction with the value of 52.10 kcal mol⁻¹ for H; the data correspond to the standard temperature of 298.15 K. The individual bond dissociation enthalpy values computed from isodesmic enthalpies of formation are given in Table 2.4

We compare the bond energies against similar bond energies in a ketone; and for purposes of comparison we evaluate and use the RC--H bond energies in acetone as 95.8 kcal mol⁻¹. The bond dissociation energies for H--CH₂C(=O)CH₂NO₂ and H--CH₂C(=O)CH₂ONO are the same bond energies as in acetone. The bond energies for *cc(=o)cjno2* radical site are 95.46 kcal mol⁻¹; ~5 kcal mol⁻¹ increase from bond energies in secondary carbon in methyl ethyl ketone (MEK). This is due to resonance of the

radical between this alpha carbon and the carbonyl carbon. Kemnitz et al.⁴⁷ also find correlation between the internal rotor barrier and resonance in C--N atom for imides.

Nitro and nitrite group substitution for a hydrogen atom on the carbonyl carbon in acetaldehyde increased bond energies ~ 1 kcal mol⁻¹ in H--CH₂C(=O)NO₂ (95.9 kcal mol⁻¹) and ~ 4 kcal mol⁻¹ for H--CH₂C(=O)ONO (98.34 kcal mol⁻¹).

The RC--H bond energies in nitroethylene, H--CH=CHNO₂, is 115.04 kcal mol⁻¹ and vinyl nitrite, H--CH=CHONO is 114.43 kcal mol⁻¹ which is ~ 4 kcal mol⁻¹ higher than that in ethylene. The RC--H bond energies in CH₂=C(--H)NO₂ (114.85 kcal mol⁻¹) increased ~ 6 kcal mol⁻¹ compared to the secondary bond energies in propylene. This results from the NO₂, ONO (electron withdrawing group) drawing an electron through the pi bond making the CH₂ carbon more electrophilic (carbon atom more positive) and subsequently the O₂NCH=CH--H bond stronger.

The *cc(=o)cjono* and *c=cjono* molecules do not exist because the RO--NO bond at 43 kcal mol⁻¹ is much weaker than the carbonyl π bond (~ 80 kcal mol⁻¹) being formed in CH₃C(=O)CH(=O) and ketene, CH₂=C=O. These molecules with the radical site adjacent to the *-ono* group dissociate to form a carbonyl and NO radical immediately upon their formation.

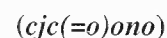
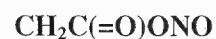
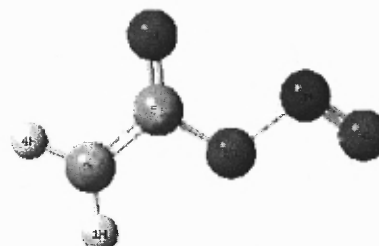
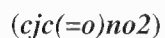
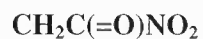
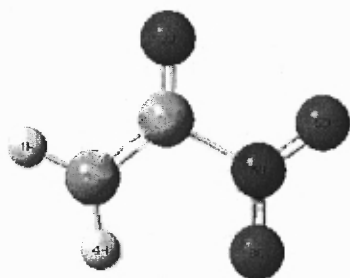
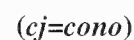
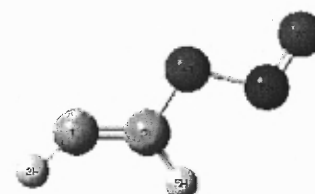
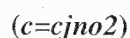
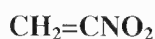
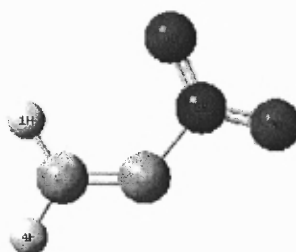
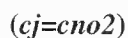
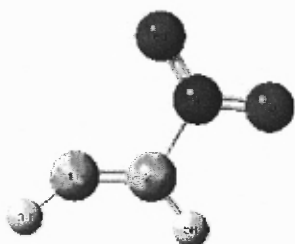
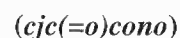
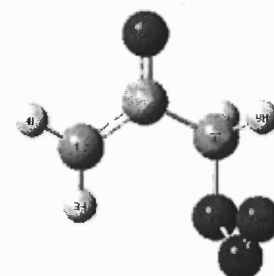
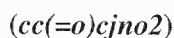
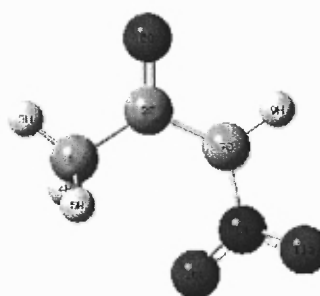
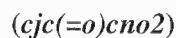
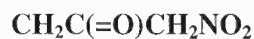
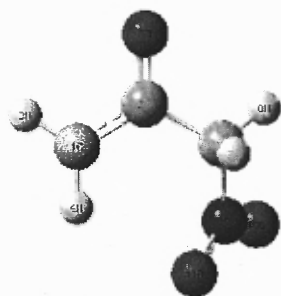


Figure 2.2 Structures and used nomenclature of the lowest energy conformers of radicals corresponding to the loss of a hydrogen atom from parent molecules (see Table C2.2-C2.15, appendix C, for details).

Table 2.4 Reaction Enthalpies at 298 K for Radicals, Calculated Enthalpies of Formation and Bond Energy^a

Work Reactions		$\Delta H^\circ(298)$ kcal mol ⁻¹				
		B3LYP			CBS-QB3	
		6-31G(d,p)	6-31+G(2d,2p)			
CH₃C(=O)CH₂NO₂ system						
CH₂C(=O)CH₂NO₂ (<i>cjc(=o)cno2</i>)						
<i>cjc(=o)cno2</i>	+ CH ₃ C(=O)CH ₃	→	<i>cc(=o)cno2</i> + C.H ₂ C(=O)CH ₃	-7.97	-7.03	-8.16
<i>cjc(=o)cno2</i>	+ CH ₃ C(=O)H	→	<i>cc(=o)cno2</i> + C.H ₂ C(=O)H	-7.53	-6.8	-6.98
<i>cjc(=o)cno2</i>	+ C ₃ H ₈	→	<i>cc(=o)cno2</i> + C.H ₂ CH ₂ CH ₃	-9.67	-6.71	-8.41
Average				-8.39	-6.85	-7.85
Bond Energy H--CH₂C(=O)CH₂NO₂				94.89	96.01	95.83
CH₃C(=O)CHNO₂ (<i>cc(=o)cjno2</i>)						
<i>cc(=o)cjno2</i>	+ CH ₃ C(=O)CH ₃	→	<i>cc(=o)cno2</i> + C.H ₂ C(=O)CH ₃	-10.35	-9.05	-9
<i>cc(=o)cjno2</i>	+ CH ₃ C(=O)H	→	<i>cc(=o)cno2</i> + C.H ₂ C(=O)H	-9.9	-8.82	-7.81
<i>cc(=o)cjno2</i>	+ CH ₃ NO ₂	→	<i>cc(=o)cno2</i> + C.H ₂ NO ₂	-9.65	-7.07	-7.86
Average				-9.97	-8.32	-8.22
Bond Energy CH₃C(=O)CH(--H)NO₂				93.31	94.55	95.46
CH₃C(=O)CH₂ONO system						
CH₂C(=O)CH₂ONO (<i>cjc(=o)cono</i>)						
<i>cjc(=o)cono</i>	+ CH ₃ C(=O)CH ₃	→	<i>cc(=o)cono</i> + C.H ₂ C(=O)CH ₃	-9.25	-7.43	-8.3
<i>cjc(=o)cono</i>	+ CH ₃ C(=O)H	→	<i>cc(=o)cono</i> + C.H ₂ C(=O)H	-8.81	-7.19	-7.12
<i>cjc(=o)cono</i>	+ C ₃ H ₈	→	<i>cc(=o)cono</i> + C.H ₂ CH ₂ CH ₃	-10.96	-7.1	-8.54
Average				-9.67	-7.24	-7.99
Bond Energy H--CH₂C(=O)CH₂ONO				94.32	96.34	95.37

Table 2.4 (Continued)

Work Reactions		$\Delta_f H^\circ(298)$ kcal mol ⁻¹				
		B3LYP			CBS-QB3	
		6-31G(d,p)	6-31+G(2d,2p)			
CH₂=CHNO₂ system						
CH=CHNO₂ (cj=cno2)						
cj=cno2	+ C ₂ H ₄	---	C.H=CH ₂	70.32	70.66	70.73
cj=cno2	+ C ₃ H ₆	---	C.H=CHCH ₃	70.38	71.73	70.97
cj=cno2	+ C ₃ H ₆	---	CH ₂ =CHC.H ₂	70.34	71.46	69.9
			Average	70.35	71.28	70.54
			Bond Energy H--CH=CHNO₂	114.85	115.79	115.04
CH₂=CNO₂ (c=cjno2)						
c=cjno2	+ C ₂ H ₄	---	C.H=CH ₂	70.32	70.66	70.73
c=cjno2	+ C ₃ H ₆	---	CH ₂ =C.CH ₃	69.81	71.02	69.33
c=cjno2	+ C ₃ H ₈	---	CH ₃ C.HCH ₃	71.92	73.3	70.97
			Average	70.68	71.66	70.35
			Bond Energy CH₂=C(--H)NO₂	115.19	116.17	114.85
CH₂=CHONO system						
CH=CHONO (cj=cono)						
cj=cono	+ C ₂ H ₄	---	C.H=CH ₂	69.75	70.09	69.76
cj=cono	+ C ₃ H ₆	---	C.H=CHCH ₃	69.82	71.16	70
cj=cono	+ C ₃ H ₆	---	CH ₂ =CHC.H ₂	69.77	70.89	68.93
			Average	69.78	70.71	69.56
			Bond Energy H--CH=CHONO	114.65	115.58	114.43

Table 2.4 (Continued)

Work Reactions		$\Delta_f H^\circ(298)$ kcal mol ⁻¹		
		B3LYP		
		6-31G(d,p)	6-31+G(2d,2p)	CBS-QB3
CH₃C(=O)NO₂ system				
CH₂C(=O)NO₂ (cjc(=o)no2)				
cjc(=o)no2	+ CH ₃ C(=O)CH ₃	---> cc(=o)no2	+ C.H ₂ C(=O)CH ₃	-2.23 -1.86 -2.04
cjc(=o)no2	+ CH ₃ C(=O)H	---> cc(=o)no2	+ C.H ₂ C(=O)H	-2.27 -0.14 0.23
cjc(=o)no2	+ CH ₂ =CHCH ₃	---> cc(=o)no2	+ CH ₂ =CHC.H ₂	-2.82 -0.72 -1.79
			Average	-2.14 -1.28 -1.57
Bond Energy H--CH₂C(=O)NO₂				95.34 96.19 95.9
CH₃C(=O)ONO system				
CH₂C(=O)ONO (cjc(=o)ono)				
cjc(=o)ono	+ CH ₃ C(=O)CH ₃	---> cc(=o)ono	+ C.H ₂ C(=O)CH ₃	-12.5 -12.7 -12.41
cjc(=o)ono	+ CH ₃ C(=O)H	---> cc(=o)ono	+ C.H ₂ C(=O)H	-10.55 -10.97 -10.14
cjc(=o)ono	+ CH ₂ =CHCH ₃	---> cc(=o)ono	+ CH ₂ =CHC.H ₂	-13.1 -11.56 -12.16
			Average	-12.42 -12.11 -11.93
Bond Energy H--CH₂C(=O)ONO				97.86 98.17 98.34

^aReaction enthalpies include thermal correction and zero-point energy

Table 2.5 Summary of $\Delta_f H_{298}$ and Bond Energy Values for Nitrocarbonyls and Nitroolefins and their Carbon Radicals^a (in kcal mol⁻¹).

Species	$\Delta_f H_{298}$ (in bold) and BDE (in italic)		
	B3LYP		CBS-QB3
	6-31G(d,p)	6-31+G(2d,2p)	
CH₃C(=O)CH₂NO₂	-51.18	-50.86	-51.58
<i>cjc(=o)cno2</i>	-8.39	-6.85	-7.85
Bond Energy H--CH ₂ C(=O)CH ₂ NO ₂	<i>94.89</i>	<i>96.01</i>	<i>95.83</i>
<i>cc(=o)cjno2</i>	-9.97	-8.32	-8.22
Bond Energy CH ₃ C(=O)CH(--H)NO ₂	<i>93.31</i>	<i>94.55</i>	<i>95.46</i>
CH₃C(=O)CH₂ONO	-51.89	-51.48	-51.26
<i>cjc(=o)cono</i>	-9.67	-7.24	-7.99
Bond Energy H--CH ₂ C(=O)CH ₂ ONO	<i>94.32</i>	<i>96.34</i>	<i>95.37</i>
CH₂=CHNO₂	6.34	7.17	7.59
<i>cj=cno2</i>	70.35	71.28	70.54
Bond Energy H--CH=CHNO ₂	<i>114.85</i>	<i>115.79</i>	<i>115.04</i>
<i>c=cjno2</i>	70.68	71.66	70.35
Bond Energy CH ₂ =C(--H)NO ₂	<i>115.19</i>	<i>116.17</i>	<i>114.85</i>
CH₂=CHONO	6.2	4.97	7.23
<i>cj=cono</i>	69.78	70.71	69.56
Bond Energy H--CH=CHONO	<i>114.65</i>	<i>115.58</i>	<i>114.43</i>
CH₃C(=O)NO₂	-47.21	-44.96	-45.36
<i>cjc(=o)no2</i>	-2.14	-1.28	-1.57
Bond Energy H--CH ₂ C(=O)NO ₂	<i>95.34</i>	<i>96.19</i>	<i>95.9</i>
CH₃C(=O)ONO	-58.36	-57.29	-58.17
<i>cjc(=o)ono</i>	-12.42	-12.11	-11.93
Bond Energy H--CH ₂ C(=O)ONO	<i>97.86</i>	<i>98.17</i>	<i>98.34</i>

^a Radicals are represented by abbreviated formulas, for simplicity; j represents a radical site.

2.4.3 Internal Rotation Potentials

Rotation about the C-C, C-O, C-NO₂, C-ONO and O-NO bonds in the target molecules are studied. Energy profiles for internal rotations were calculated to determine energies of the rotational conformers and interconversion barriers along with contributions to the

entropy and heat capacity for the low barrier (below 4.5 kcal mol⁻¹) rotors. Frequencies calculated by the Gaussian code are examined by viewing the vibration mode movement; the contributions from frequencies corresponding to internal rotations are excluded from the entropy and heat capacity and replaced with a more accurate estimate of S and $C_p(T)$ from the internal rotor contributions. The total energies as a function of the dihedral angles were computed at the B3LYP/6-31G(d,p) level of theory by scanning the torsion angles between 0° and 360° in steps of 15°, while all remaining coordinates were fully optimized. All potentials were re-scanned when a lower energy conformer is found, relative to the initial low energy conformer. The total energy corresponding to the most stable molecular conformer was arbitrarily set to zero and thus used as a reference point to plot the potential barriers. The resulting potential energy barriers for internal rotations in the stable non-radical and radical molecules are shown in Figs. 2.3.1–2.3.14. Dihedral angle used in optimize structure are shown in parenthesis

The calculated rotational barriers of methyl groups all show the symmetrical three-fold symmetry with the barrier between 1.0 and 1.5 kcal mol⁻¹ which is a little bit lower compare to typical alkyl methyl rotations which ranging between 2.7 and 3.0 kcal mol⁻¹. The C-NO₂ rotors in nitroacetone and nitroacetate exhibited low, 2-fold symmetric barriers of 1.4, and 2.0 kcal mol⁻¹ heights, respectively while the potential for nitroethylene had 2-fold symmetry with a barrier of 6.5 kcal mol⁻¹. RO--NO internal rotors in 2 propane nitrite and vinyl nitrite show symmetric 2-fold high barriers of 13 kcal mol⁻¹ while the potential in acetyl nitrite had a 2-fold barrier of 3.0 and 4.5 kcal mol⁻¹.

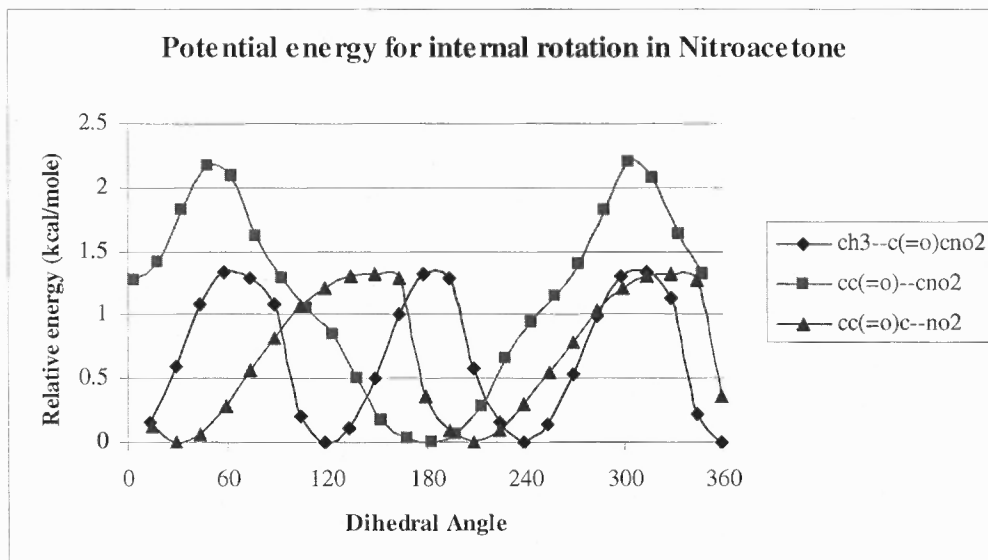


Figure 2.3.1 Potential Energy Profiles for Internal Rotations in Nitroacetone.

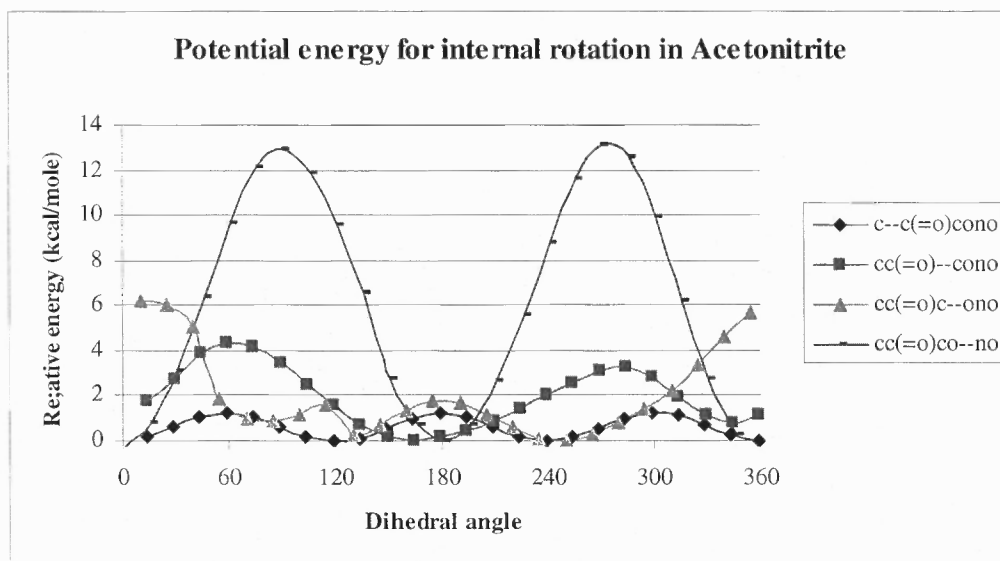


Figure 2.3.2 Potential Energy Profiles for Internal Rotations in 2 propanone nitrile.

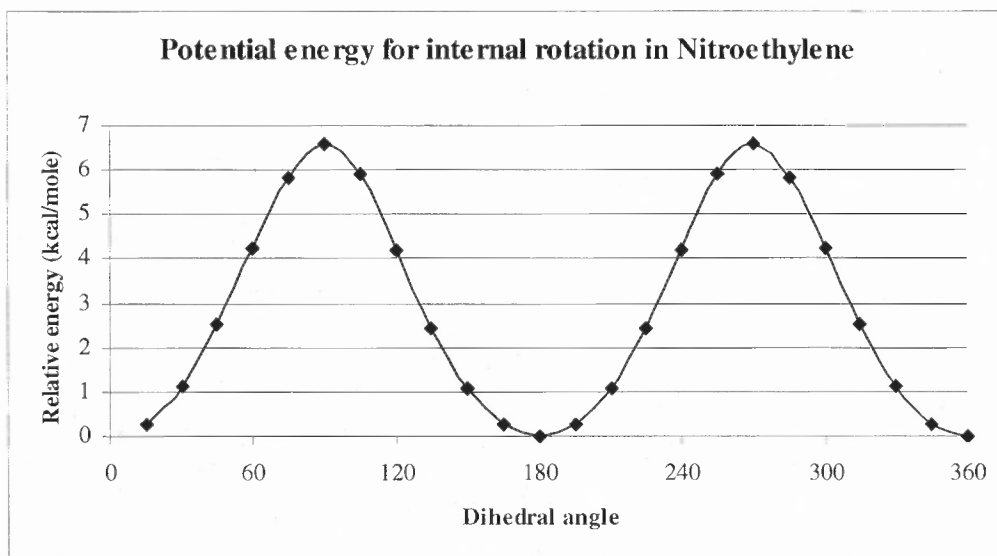


Figure 2.3.3 Potential Energy Profiles for Internal Rotations in Nitroethylene.

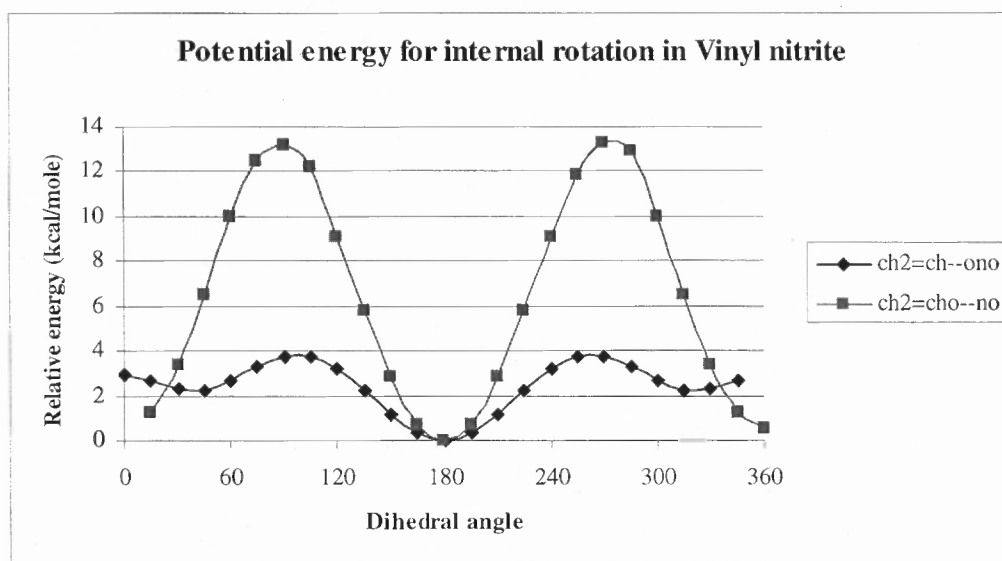


Figure 2.3.4 Potential Energy Profiles for Internal Rotations in Vinyl nitrite.

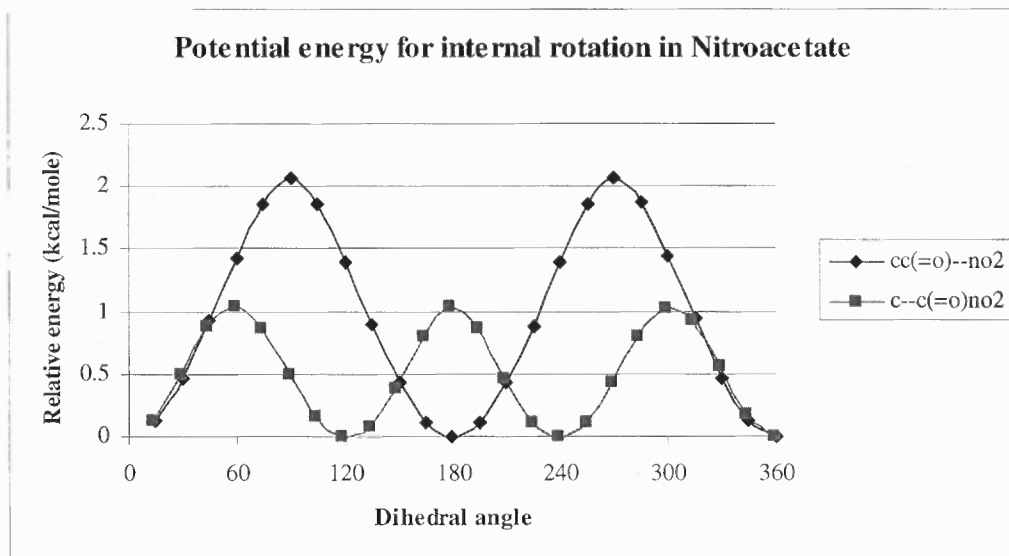


Figure 2.3.5 Potential Energy Profiles for Internal Rotations in Nitroacetate.

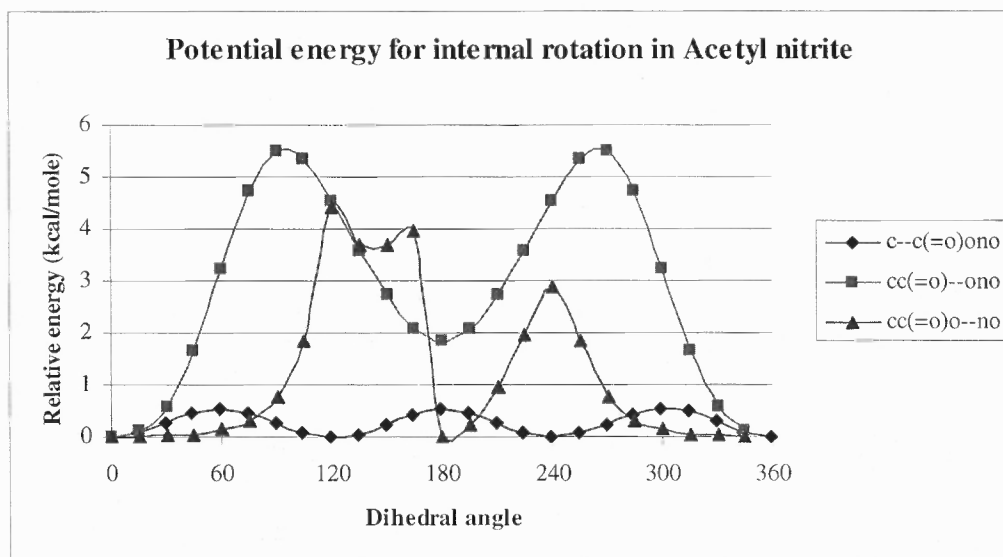
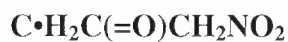


Figure 2.3.6 Potential Energy Profiles for Internal Rotations in Acetyl nitrite.



cjc(=o)--cno2 rotor and *--NO₂* rotor barrier are similar to that in the parent *cjc(=o)cno2*. The barrier for the *cj--c(=o)cno2* rotor of the methyl radical site is significantly increased (to 13 kcal mol⁻¹) and distorted two potential compared to a 3-fold barrier for the parent. This barrier increase (11.6 kcal mol⁻¹) suggests a high degree of resonance between the carbon radical and the carbonyl oxygen; this is interpreted as the difference between the barrier of the parent and was also observed by Kemnitz et al⁴⁷.

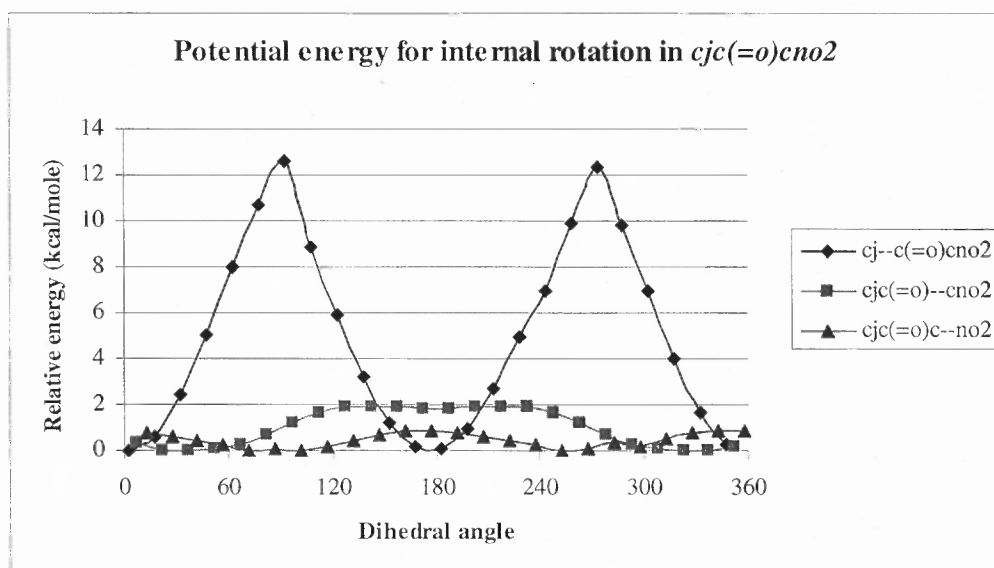


Figure 2.3.7 Potential Energy Profiles for Internal Rotations in *cjc(=o)cno2*



The --NO₂ rotor in *cc(=o)cjno2* is increased from 2.1 kcal mol⁻¹ in nitroacetone to 8 kcal mol⁻¹ in radical, this is reflected in the 6 kcal mol⁻¹ resonance. The *cc(=o)--cjno2* rotor has a 2-fold potential with the barrier at 3.1 kcal mol⁻¹ while the methyl rotor is similar to that in the parent.

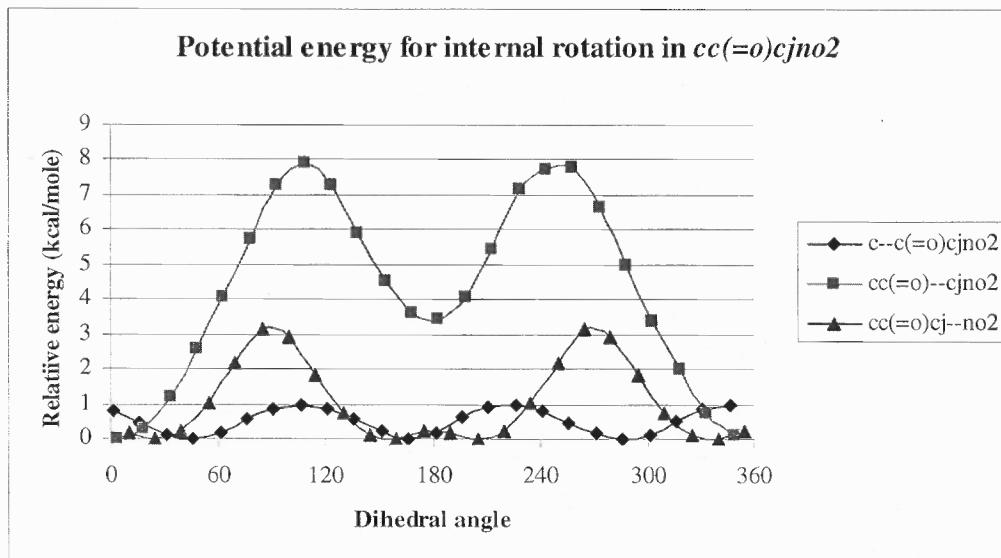


Figure 2.3.8 Potential Energy Profiles for Internal Rotations in *cc(=o)cjno2*

$\text{C}\cdot\text{H}_2\text{C}(=\text{O})\text{CH}_2\text{ONO}$

There are significant differences in internal rotor potentials between the *cjc(=o)cono* radical (*cis* configuration) and the parent (*trans* configuration). The *cjc(=o)c--ono* rotor has a 2-fold barrier with the barrier of 9 and 3 kcal mol⁻¹ while the *cjc(=o)--cono* rotor has a distorted one potential at 3.5 kcal mol⁻¹. The parent has a two fold potential. The *cjc(=o)co--no* rotor is similar to that in the parent with a two fold potential and very high barrier (13 kcal mol⁻¹). The barrier for the *cj--c(=o)cono* rotor of the methyl radical site is increased from 1.5 kcal mol⁻¹ in the parent to 12 kcal mol⁻¹ in this radical. This is reflected in the 10.5 kcal mol⁻¹ resonance.

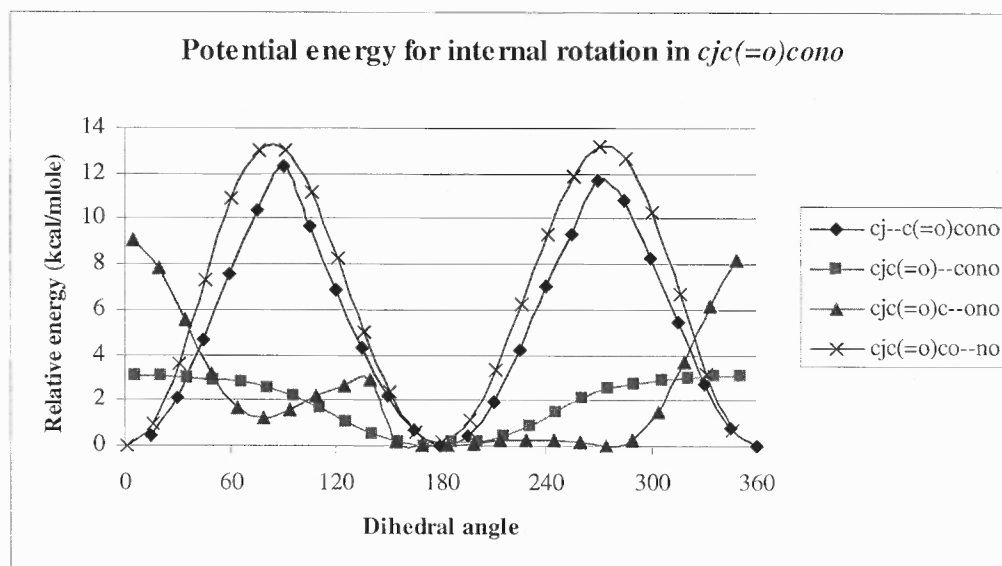


Figure 2.3.9. Potential energy profile for internal rotations in *cjc(=o)cono*



The --NO₂ rotor in *cj=cno2* has a 2-fold barrier with the barriers at 5 kcal mol⁻¹ compared to the parent with a 2-fold barrier at 6.5 kcal mol⁻¹

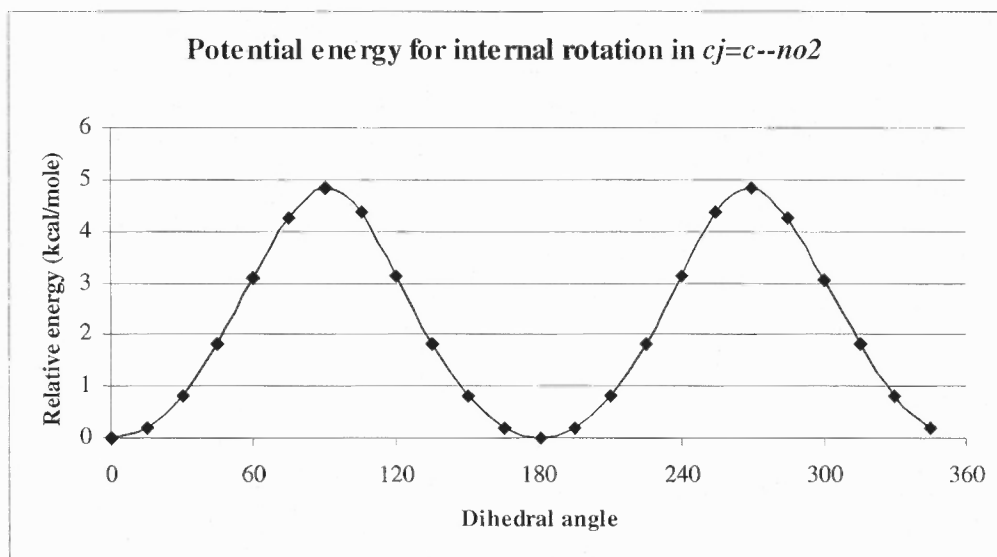


Figure 2.3.10 Potential Energy for Internal Rotation in *cj=cno2*



The --NO₂ rotor exhibits a 2-fold barrier with some distortion of the symmetric 2-fold potential of the parent and the barriers is decreased from 6.5 kcal mol⁻¹ in the parent to 2.5 kcal mol⁻¹ in this radical.

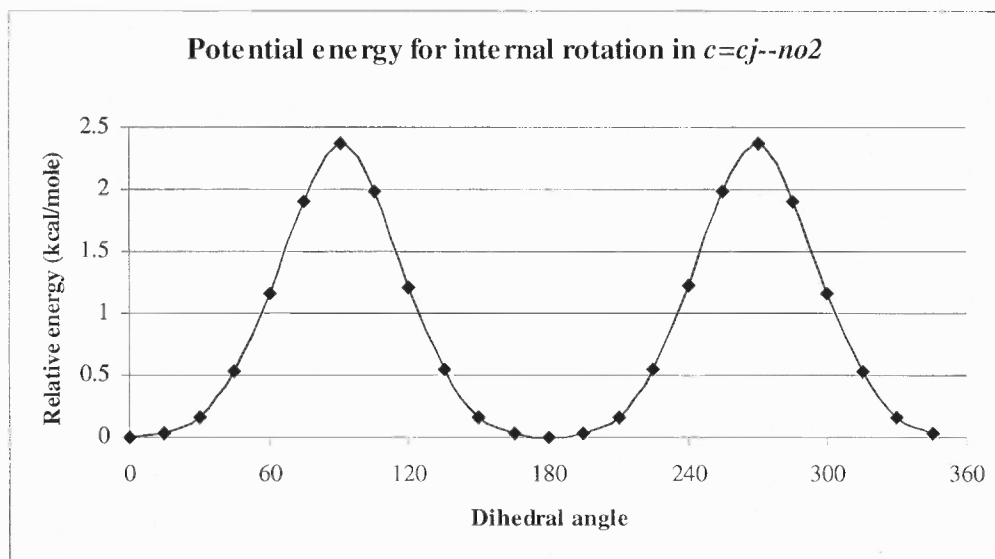


Figure 2.3.11 Potential Energy for Internal Rotation in *c=cjno2*

C•H=CHONO

All internal rotor in $cj=cono$ are similar to those in the parent vinyl nitrite. The $cj=co--no$ rotor is similar to that in the parent with a two fold potential and very high barrier (13.5 kcal mol⁻¹) while the $cj=c--ono$ rotor has a three fold potential with one at barrier at 2 kcal mol⁻¹ and two barriers at 4 kcal mol⁻¹.

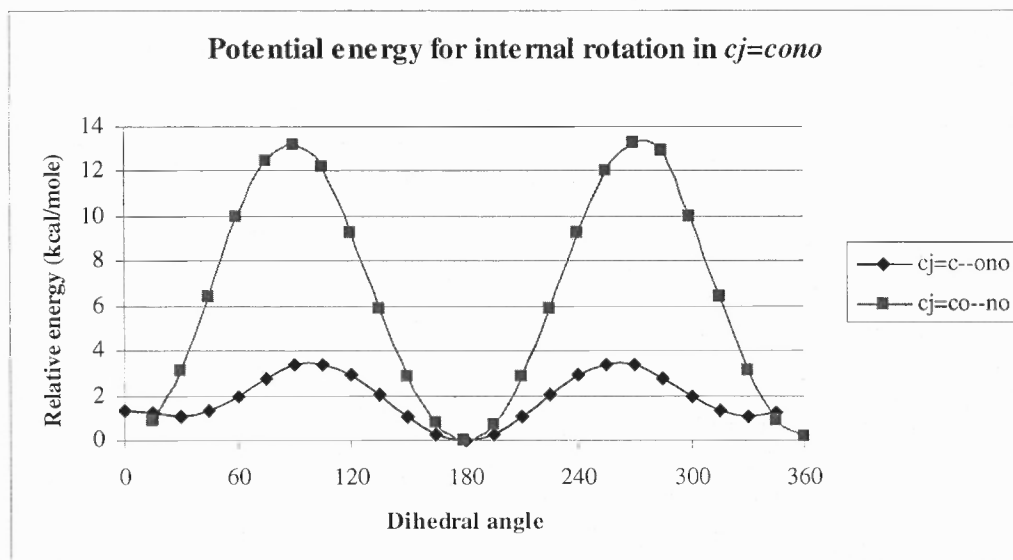


Figure 2.3.12 Potential Energy for Internal Rotation in $cj=cono$

$\text{C}\cdot\text{H}_2\text{C}(=\text{O})\text{NO}_2$

The barrier for the *cj--c(=o)no2* rotor of the methyl radical site is significantly increased (to 12 kcal mol^{-1}) and distorted two potential compared to the three fold for the parent. This barrier increase (11 kcal mol^{-1}) suggests a high degree of resonance between the carbon radical and the carbonyl oxygen. The *cjc(=o)—no2* rotor has a 2-fold barrier with the barrier of 4 kcal mol^{-1}

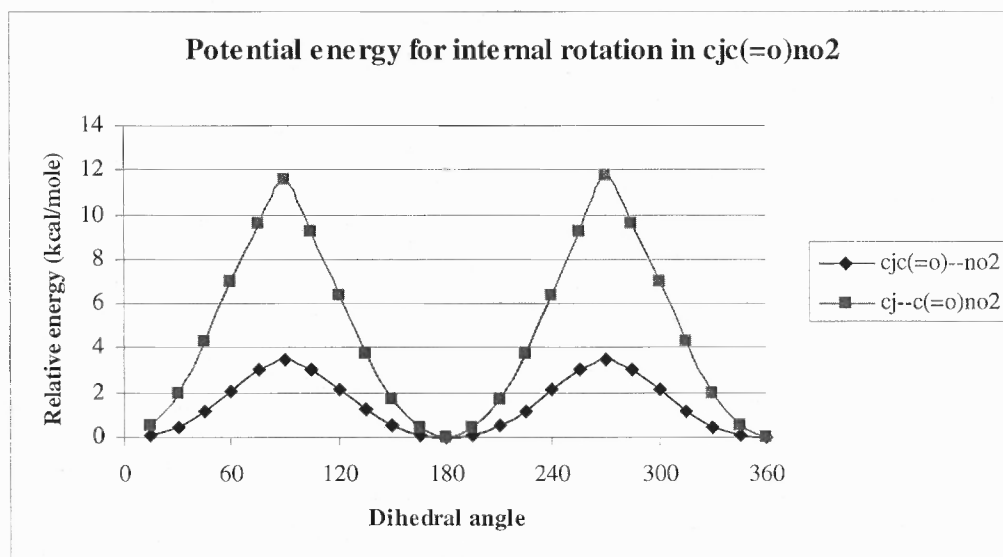


Figure 2.3.13 Potential Energy for Internal Rotation in *cjc(=o)no2*

$\text{C}\cdot\text{H}_2\text{C}(=\text{O})\text{ONO}$

The barrier for the $cj\text{-}c(=\text{o})\text{ono}$ rotor of the methyl radical site is significantly increased (to 9 kcal mol^{-1}) and distorted two potential compared to three fold for the parent. This barrier increase ($8.5 \text{ kcal mol}^{-1}$) suggests a high degree of resonance between the carbon radical and the carbonyl oxygen. The $cjc(=\text{o})\text{-}ono$ and $cjc(=\text{o})\text{o-no}$ rotor barriers increase $\sim 1 \text{ kcal mol}^{-1}$ with two fold compare to that in the parent.

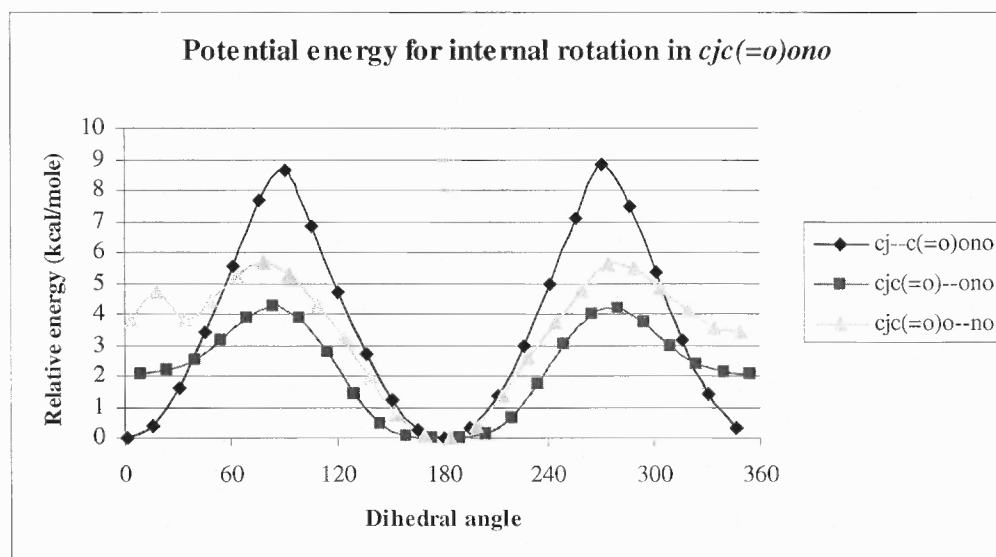


Figure 2.3.14 Potential Energy for Internal Rotation in $cjc(=\text{o})\text{ono}$

2.4.4 Entropy and Heat Capacity Data

Entropy and heat capacity contributions as a function of temperature are determined from the calculated structures, moments of inertia, vibration frequencies, symmetry, electron degeneracy, number of optical isomers and the known mass of each molecule. The calculations use standard formulas from statistical mechanics for the contributions of translation, external rotation and vibrations using the “SMCPS” program.⁴² This program utilizes the rigid-rotor-harmonic oscillator approximation from the frequencies along with

moments of inertia from the optimized CBS-QB3 structures, *viz.* B3LYP/6-311G(2d,d,p) level. Contributions from internal rotors (see IR in Table 2.4) using the Pitzer-Gwinn formalism^{45, 46} are substituted for contributions from internal rotor torsion frequencies where barriers were determined to be below 4.5 kcal mol⁻¹. These entropy and heat capacity data are needed to determine dependence of the enthalpy, entropy, Gibbs Energy and equilibrium constants with temperature. Entropy and heat capacity calculation were performed using complete basis set -QB3 determined geometries and harmonic frequencies summarized in Table 2.4

Table 2.6 Ideal Gas-phase Thermodynamic Property vs Temperature^a

T(K)	<i>cc(=o)cno2</i>		<i>cjc(=o)cno2</i>		<i>cc(=o)cjno2</i>		<i>cc(=o)cono</i>		<i>cjc(=o)cono</i>	
	C _p (T)	S ^o (T)(6) ^b	C _p (T)	S ^o (T)(2)	C _p (T)	S ^o (T)(6)	C _p (T)	S ^o (T)(3)	C _p (T)	S ^o (T)(1)
5	7.95	31.22	7.95	34.70	7.95	32.56	7.95	32.82	7.95	36.10
50	8.27	49.59	8.15	53.04	8.75	51.09	8.85	51.35	9.79	55.74
100	9.76	55.73	9.75	59.09	11.03	57.83	11.98	58.41	12.01	63.12
150	12.02	60.09	12.47	63.53	13.66	62.78	15.13	63.86	15.30	68.58
200	14.69	63.90	15.55	67.53	16.49	67.09	18.12	68.62	18.72	73.45
250	17.55	67.47	18.68	71.33	19.37	71.07	21.04	72.97	21.98	77.97
298	20.38	90.42	21.61	89.87	22.12	86.45	23.80	88.80	24.92	88.76
300	26.25	70.92	25.34	75.00	26.01	74.85	27.92	77.05	27.38	82.24
350	23.41	74.30	24.63	78.56	24.97	78.47	26.70	80.94	27.88	86.31
400	31.24	77.60	30.49	82.02	31.13	81.97	33.14	84.68	32.75	90.20
500	35.73	83.98	34.82	88.62	35.41	88.61	37.65	91.74	37.04	97.48
600	39.55	90.05	38.35	94.78	38.87	94.79	41.39	98.31	40.42	104.16
700	42.68	95.76	41.20	100.51	41.68	100.52	44.42	104.43	43.10	110.31
800	45.45	101.14	43.57	105.84	43.98	105.86	47.10	110.14	45.35	115.98
900	47.68	106.19	45.49	110.81	45.86	110.83	49.17	115.48	47.15	121.24
1000	49.70	110.95	47.18	115.45	47.52	115.47	51.19	120.48	48.77	126.13
1200	52.69	119.68	49.71	123.88	49.94	123.92	53.93	129.62	51.11	134.99
1300	53.92	123.68	50.74	127.73	50.93	127.77	55.09	133.81	52.08	139.02
1400	54.98	127.49	51.64	131.37	51.80	131.42	56.10	137.77	52.93	142.83
1500	56.05	131.10	52.50	134.82	52.71	134.87	57.33	141.53	53.81	146.43
2000	56.11	146.79	53.08	149.72	53.13	149.78	58.21	157.84	55.19	161.94
2500	57.89	159.51	54.55	161.73	54.59	161.80	59.95	171.03	56.62	174.42
3000	58.94	170.16	55.42	171.76	55.45	171.84	60.99	182.06	57.47	184.83
3500	59.61	179.30	55.97	180.34	56.00	180.43	61.64	191.51	58.01	193.73
4000	60.06	187.29	56.34	187.84	56.36	187.93	62.08	199.77	58.37	201.50
4500	60.37	194.38	56.61	194.49	56.62	194.58	62.38	207.10	58.62	208.38
5000	60.60	200.76	56.79	200.47	56.81	200.56	62.61	213.68	58.80	214.57

Table 2.6 (Continued)

T(K)	<i>c=cno2</i>		<i>cj=cno2</i>		<i>c=cjno2</i>		<i>c=cono</i>		<i>cj=cono</i>	
	Cp(T)	S°(T)(1)	Cp(T)	S°(T)(1)	Cp(T)	S°(T)(2)	Cp(T)	S°(T)(1)	Cp(T)	S°(T)(1)
5	7.95	31.25	7.95	32.48	7.95	31.14	7.95	30.88	7.95	31.98
50	8.90	49.93	9.15	51.36	8.00	49.45	8.92	49.52	8.90	50.62
100	10.09	56.47	10.39	58.08	8.79	55.19	10.57	56.23	10.55	57.30
150	11.52	60.81	11.89	62.56	10.20	59.00	12.09	60.79	12.23	61.88
200	13.34	64.36	13.79	66.23	11.92	62.17	13.78	64.49	14.07	65.65
250	15.37	67.55	15.81	69.52	13.73	65.02	15.61	67.76	15.92	68.98
298	17.37	70.41	17.68	72.45	15.44	73.37	17.41	76.03	17.58	77.34
300	17.45	70.53	17.76	72.57	17.78	67.67	19.76	70.77	19.94	72.03
350	19.49	73.37	19.55	75.44	17.19	70.19	19.29	73.59	19.20	74.87
400	21.40	76.09	21.15	78.15	20.82	72.58	23.31	76.28	22.90	77.52
500	24.74	81.23	23.84	83.17	23.27	77.05	26.19	81.28	25.11	82.37
600	27.45	85.98	25.94	87.70	25.24	81.15	28.48	85.86	26.78	86.71
700	29.64	90.38	27.60	91.82	26.86	84.91	30.31	90.07	28.06	90.63
800	31.43	94.45	28.95	95.60	28.13	88.37	31.84	93.97	29.19	94.21
900	32.93	98.24	30.05	99.07	29.20	91.58	33.10	97.58	30.04	97.50
1000	34.19	101.77	30.98	102.28	30.12	94.57	34.20	100.94	30.86	100.54
1200	36.18	108.18	32.42	108.06	31.50	99.96	35.89	107.05	31.98	106.01
1300	36.97	111.11	32.99	110.68	32.07	102.40	36.58	109.84	32.45	108.48
1400	37.65	113.87	33.48	113.14	32.58	104.71	37.17	112.47	32.85	110.81
1500	38.25	116.49	33.90	115.46	32.99	106.89	37.77	114.97	33.35	113.01
2000	40.27	127.80	35.34	125.43	33.32	116.28	38.39	125.74	33.44	122.44
2500	41.38	136.91	36.12	133.41	34.12	123.81	39.46	134.43	34.19	129.99
3000	42.04	144.51	36.58	140.03	34.59	130.07	40.10	141.69	34.64	136.26
3500	42.46	151.03	36.88	145.70	34.89	135.43	40.51	147.90	34.92	141.62
4000	42.74	156.72	37.07	150.63	35.08	140.10	40.78	153.33	35.11	146.30
4500	42.94	161.76	37.21	155.01	35.22	144.24	40.98	158.14	35.24	150.44
5000	43.08	166.29	37.31	158.93	35.32	147.95	41.11	162.47	35.34	154.16

Table 2.6 (Continued)

T(K)	<i>cc(=o)no2</i>		<i>cjc(=o)no2</i>		<i>cc(=o)ono</i>		<i>cjc(=o)ono</i>	
	C _p (T)	S°(T)(6)	C _p (T)	S°(T)(2)	C _p (T)	S°(T)(3)	C _p (T)	S°(T)(1)
5	7.95	29.61	7.95	33.01	7.95	31.17	7.97	34.56
50	8.00	47.92	7.99	51.32	9.87	50.93	10.04	55.15
100	9.17	53.73	9.27	57.13	11.51	58.26	11.92	62.62
150	11.34	57.84	11.86	61.35	13.34	63.26	14.27	67.89
200	13.64	61.41	14.56	65.13	15.32	67.36	16.67	72.32
250	15.86	64.69	17.05	68.65	17.32	70.98	18.93	76.28
298	17.91	79.82	19.21	77.82	19.21	85.19	20.91	85.75
300	21.68	67.77	21.60	71.95	22.68	74.31	23.23	79.91
350	20.03	70.69	21.30	75.08	21.17	77.42	22.83	83.28
400	25.18	73.48	25.42	78.04	26.37	80.36	26.79	86.43
500	28.25	78.75	28.34	83.52	29.51	85.83	29.50	92.19
600	30.86	83.62	30.58	88.50	32.08	90.83	31.56	97.34
700	32.97	88.14	32.28	93.04	34.13	95.43	33.15	101.99
800	34.91	92.34	33.73	97.20	35.91	99.69	34.43	106.22
900	36.21	96.26	34.83	101.03	37.34	103.65	35.50	110.11
1000	37.80	99.92	35.83	104.59	38.59	107.35	36.34	113.70
1200	39.39	106.60	37.21	110.98	40.49	114.06	37.74	120.14
1300	40.17	109.65	37.77	113.88	41.25	117.13	38.27	123.06
1400	40.84	112.53	38.27	116.60	41.90	120.02	38.72	125.80
1500	42.07	115.27	38.82	119.17	42.52	122.77	39.09	128.38
2000	42.11	127.08	39.10	130.20	42.18	134.61	39.19	139.44
2500	43.28	136.61	39.96	139.03	43.33	144.16	40.01	148.28
3000	43.97	144.57	40.46	146.36	44.00	152.12	40.50	155.62
3500	44.41	151.38	40.78	152.62	44.43	158.94	40.81	161.89
4000	44.70	157.33	40.99	158.08	44.72	164.89	41.01	167.35
4500	44.90	162.61	41.14	162.92	44.92	170.17	41.16	172.19
5000	45.05	167.35	41.25	167.26	45.06	174.91	41.27	176.53

^aThermodynamic properties are referred to standard state of an ideal gas at 1 atm. S°(T) and C_p°(T) are in cal mol⁻¹ K⁻¹

^bSymmetry numbers used for calculation of S°(T) are in parenthesis

2.4.5 Group Values for use in the Group Additivity Method for Estimation of Thermochemical properties

Group additivity⁴³ is a straightforward and reasonably accurate calculation method to estimate thermodynamic properties of hydrocarbons and oxygenated hydrocarbons⁴⁴; it is particularly useful for application to larger molecules and for use in codes or databases for the estimation of thermochemical properties in reaction mechanism generation. In this paper, we estimate six nitrocarbonyls, nitroolefins, corresponding nitrites and eight carbon centered radicals groups by using the thermodynamic property data developed in this study, plus the alkyl-hydrocarbon groups in the literature. The fourteen groups are listed in the Table 2.7, along with standard hydrocarbon groups used.

Table 2.7 Group Thermochemical Values

Group	$\Delta_f H^\circ(298)$ (kcal mol ⁻¹)	$S^\circ(298)$ (cal mol ⁻¹ K ⁻¹)	$C_p^\circ(T)$ (cal mol ⁻¹ K ⁻¹)						
			300K	400K	500K	600K	800K	1000K	1500K
Groups developed in this study									
C/CO/H2/NO2	-10.1	48.56	14.47	17.08	19.24	21	23.54	25.32	0
C/CO/H2/ONO	-9.66	45.56	16.14	18.98	21.16	22.84	25.19	26.81	0
CD/H/NO2	1.33	42.8	12.35	15.04	17.23	18.95	21.36	22.92	0
CD/H/ONO	0.97	48.42	14.66	16.95	18.68	19.98	21.77	22.93	0
CO/C/NO2	-35.28	52.97	15.49	17.34	18.85	20.07	21.89	23.03	0
CO/C/ONO	-48.09	56.96	16.49	18.53	20.11	21.29	22.89	23.82	0
CJCDOCNO2	96.2	-2.73	-0.91	-0.75	-0.91	-1.2	-1.88	-2.52	0
CCDOCJNO2	95.83	-3.97	-0.24	-0.11	-0.32	-0.68	-1.47	-2.18	0
CJCDOCONO	95.62	-2.22	-0.54	-0.39	-0.61	-0.97	-1.75	-2.42	0
CJDCNO2	115.64	2.04	0.31	-0.25	-0.9	-1.51	-2.48	-3.21	0
CDCJNO2	114.85	4.34	0.33	-0.58	-1.47	-2.21	-3.3	-4.07	0
CJDCONO	115.02	1.31	0.18	-0.41	-1.08	-1.7	-2.65	-3.34	0
CJCDOONO	96.85	-4.18	-0.08	0.24	0.09	-0.28	-1.18	-1.97	0
CJCDOONO	99.29	-1.62	0.55	0.42	-0.01	-0.52	-1.48	-2.25	0
Known groups									
C/CO/H3	-10.08	30.41	6.19	7.84	9.4	10.79	13.02	14.77	17.58
CO/C2	-31.4	15.01	5.59	6.32	7.09	7.76	8.89	9.61	0
CD/H2	6.26	27.61	5.1	6.36	7.51	8.5	10.07	11.27	13.19

^aSymmetry number (σ) is taken into account ($S = S_{\text{int}} - R \cdot \ln \sigma$)

2.5 Conclusions

Thermodynamic properties ($\Delta_f H^\circ_{298}$, S°_{298} , and $C_p(T)$, ($5 \leq T \leq 5000$ K)) for nitrocarbonyls, nitroolefins, and corresponding nitrites are reported. Standard enthalpies of formation, $\Delta_f H^\circ_{298}$, were calculated using density functional theory and isodesmic reactions. The enthalpies of formation of acetyl nitrite were found to be ~ 12 kcal mol⁻¹ more stable (lower enthalpy) than the corresponding nitro while $\Delta_f H^\circ_{298}$ of nitroacetone is

0.3 kcal mol⁻¹ more stable than the corresponding nitrite. The $\Delta_f H^\circ_{298}$ of vinyl nitrite is 0.3 kcal mol⁻¹ more stable than the corresponding nitro. The *trans* configuration respective to C-O-N-O dihedral angles in 2 propane nitrite, vinyl nitrite and acetyl nitrite are more stable than corresponding *cis* isomer. Enthalpies of formation, entropy, $S^\circ(T)$ and heat capacity, $C_p^\circ(T)$, values are reported along with bond energies and corresponding thermochemical properties for radicals corresponding to loss of a hydrogen atom from the carbons sites. The bond dissociation energies in all species were observed to increase from 0.5 to 6 kcal mol⁻¹. Rotational barrier potentials are reported for internal rotors and hindered internal rotor contributions for $\Delta_f H^\circ_{298}$, S°_{298} , and $C_p(T)$ are calculated. Groups for use in group additivity are developed.

APPENDIX A

COMPARISON THERMOCHEMISTRY DATA

Table A1.1 compares the enthalpy, entropy and heat capacity data from this study for nitropropane, 2 nitropropane and 2 nitro, 2 methyl propane with corresponding data from Ashcraft and Green⁴⁹.

Species		$\Delta_f H^\circ(298)$ kcal mol ⁻¹	$S^\circ(298)$ cal mol ⁻¹ K ⁻¹	C_p (cal mol ⁻¹ K ⁻¹)						
				300K	400K	500K	600K	800K	1000K	1500K
<i>ccno2c</i>	A-G	-33.6	82.9	25.3	31.2	36.4	40.8	47.6	52.6	60.2
	NJIT	-33.9	82.8	25.0	30.8	35.9	40.3	47.1	52.1	59.8
<i>cccno2</i>	A-G	-29.8	85.2	24.4	30.5	35.9	40.4	47.4	52.5	60.2
	NJIT	-30.6	85.5	24.7	30.6	35.8	40.2	47.1	52.2	59.9
<i>c(c3)no2</i>	A-G	-42.6	86.8	31.6	39.1	45.6	51.0	59.2	65.2	74.5
	NJIT	-42.8	86.3	31.1	38.7	45.2	50.6	58.8	64.9	74.3
<i>cccono</i>	A-G	-27.9	87.2	27.0	32.6	37.6	42.0	48.7	53.7	61.2
	NJIT	-28.4	84.9	25.5	31.2	36.4	40.8	47.8	53.0	60.8
Group Additivity parameters										
<i>c/c3/no2</i>	A-G	-12.7	5.2	13.5	16.0	17.8	18.9	20.3	21.1	21.9
	NJIT	-12.2	5.1	12.5	15.2	17.0	18.2	19.8	20.6	21.5
<i>c/c2/h/no2</i>	A-G	-13.9	27.5	13.6	16.1	18.1	19.6	21.8	23.2	25.1
	NJIT	-13.5	27.7	12.6	15.1	17.1	18.7	21.1	22.6	24.7
<i>c/c/h2/no2</i>	A-G	-14.8	48.9	12.9	15.8	18.3	20.3	23.3	25.4	28.3
	NJIT	-15.4	49.2	13.0	15.8	18.2	20.1	23.0	25.1	28.1

NJIT – This study, A-G Ashcraft and Green Reference 49.

APPENDIX B

VIBRATION FREQUENCIES AND OPTIMIZED GEOMETRY OF NITROALKANES, ALKYL NITRITE AND THEIR RADICALS

Table B1.1 Calculated at CBS-QB3 composite, viz. B3LYP/6-311G(2d,d,p) Level
Vibration Frequencies

SYSTEM	Frequencies, cm ⁻¹									
<i>ccno2</i>	23.9	117.2	206.6	295.7	374.3	502.5	590.8	663.7	806.6	877.7
	906.3	926.3	1054.9	1113.8	1150.8	1258.0	1301.4	1360.9	1384.4	1418.4
	1424.4	1476.1	1480.0	1501.7	1510.8	1642.3	3030.9	3038.5	3072.9	3082.4
	3101.0	3105.2	3140.6							
<i>cccono</i>	72.6	111.7	164.9	238.9	336.0	367.4	401.8	712.9	768.4	852.6
	900.3	931.2	992.1	1045.2	1150.5	1178.1	1266.0	1320.0	1333.4	1409.5
	1421.9	1495.4	1501.9	1504.0	1516.7	1690.2	3025.7	3028.6	3041.2	3058.9
	3075.2	3095.8	3099.3							
<i>ccno2c</i>	31.5	220.5	253.9	267.4	304.7	340.3	530.0	635.6	749.2	863.4
	909.7	950.2	962.6	1124.0	1148.2	1203.3	1327.5	1361.4	1397.8	1402.4
	1440.4	1484.0	1492.0	1498.7	1515.6	1640.1	3041.8	3044.8	3106.6	3109.2
	3111.7	3124.1	3135.6							
<i>ccconoc</i>	38.2	181.6	206.5	219.5	285.2	322.0	427.8	477.2	605.4	792.1
	889.8	938.0	946.1	974.8	1154.7	1160.8	1205.8	1367.3	1376.6	1406.5
	1421.4	1481.6	1488.2	1495.5	1510.1	1764.9	3031.7	3035.8	3040.1	3098.7
	3105.9	3107.8	3110.5							
<i>cc(c2)no2</i>	39.9	200.8	257.5	259.8	287.4	289.6	357.6	370.4	385.0	527.7
	559.3	746.3	799.3	871.3	939.5	940.8	976.2	1052.9	1053.4	1209.5
	1258.3	1282.6	1389.5	1400.1	1407.4	1445.9	1473.0	1485.7	1492.6	1498.0
	1501.7	1523.7	1627.0	3040.1	3041.3	3048.9	3105.6	3106.6	3116.1	3130.0
	3131.4	3135.0								
<i>cc(c2)ono</i>	108.6	164.2	198.0	200.1	260.0	260.0	332.7	341.4	370.0	465.5
	482.9	580.6	766.6	807.7	922.7	930.4	966.5	970.1	1048.5	1056.6
	1214.7	1266.5	1286.0	1399.7	1401.2	1427.2	1472.0	1489.7	1489.9	1499.5
	1499.8	1522.1	1748.6	3034.7	3035.4	3042.5	3101.1	3102.6	3111.5	3113.5
	3116.1	3118.3								

Table B1.1 (Continued)

<i>cjccno2</i>	28.5	81.3	117.2	266.0	362.3	481.6	558.7	590.3	655.6	798.7
	889.0	912.7	988.6	1083.3	1119.1	1234.1	1284.6	1347.9	1357.2	1416.4
	1456.0	1471.8	1478.1	1643.3	3031.6	3067.5	3079.6	3145.6	3149.3	3253.0
<i>ccjcnno2</i>	33.7	93.9	121.4	253.5	360.1	480.9	498.2	579.3	649.8	854.7
	896.0	925.4	994.5	1133.8	1172.5	1251.9	1280.5	1375.2	1403.1	1425.7
	1469.4	1479.0	1487.1	1647.4	2976.2	3043.7	3066.7	3087.5	3129.8	3174.7
<i>cccjno2</i>	68.4	84.8	221.1	297.5	337.8	512.9	578.8	663.3	715.9	804.6
	901.8	957.4	1037.3	1101.4	1146.9	1284.0	1303.6	1321.9	1369.7	1403.3
	1465.0	1496.1	1507.7	1519.9	3040.2	3041.8	3087.0	3109.8	3129.2	3229.1
<i>cjccono</i>	72.7	100.8	128.7	167.0	334.1	365.9	402.3	500.9	710.5	763.9
	852.2	910.6	987.2	1033.3	1087.6	1147.8	1219.6	1293.8	1327.7	1403.5
	1463.2	1474.6	1506.2	1693.2	2946.7	3035.5	3052.3	3084.1	3138.9	3243.8
<i>ccjcono</i>	51.5	75.2	93.2	246.5	293.4	361.6	434.5	517.5	683.2	822.3
	873.4	926.4	949.6	1000.9	1143.6	1168.7	1255.1	1354.0	1398.1	1413.2
	1474.8	1483.8	1491.2	1678.8	2965.5	3033.9	3038.9	3087.8	3091.6	3172.8
<i>cjc(no2)c</i>	26.8	168.3	221.1	252.4	303.0	347.9	493.0	553.6	624.2	752.2
	846.7	889.9	938.8	1038.8	1149.2	1188.2	1275.2	1363.3	1390.8	1416.2
	1462.8	1490.2	1498.2	1644.5	3047.1	3098.4	3114.1	3133.9	3145.8	3258.3
<i>ccj(no2)c</i>	40.9	41.1	100.5	273.4	307.6	375.7	547.0	593.9	684.1	830.9
	927.7	964.8	994.5	1039.9	1240.1	1301.3	1318.4	1399.9	1415.5	1450.3
	1458.4	1474.5	1480.7	1518.7	3008.0	3011.4	3064.1	3064.6	3125.0	3132.5
<i>cjc(ono)c</i>	70.6	155.6	217.6	237.4	291.0	337.8	405.7	474.7	598.8	673.9
	770.5	875.8	931.7	934.2	1043.6	1159.1	1193.8	1337.3	1370.2	1413.1
	1458.5	1488.3	1497.1	1671.8	3039.5	3074.9	3110.1	3116.4	3143.8	3257.4
<i>cjc(c2)no2</i>	42.0	191.5	214.8	254.9	263.1	274.8	336.9	355.8	391.5	498.3
	520.3	631.6	722.5	804.4	846.6	925.4	969.9	1005.9	1039.2	1141.5
	1255.3	1300.0	1380.5	1398.0	1422.3	1471.0	1480.9	1491.1	1501.7	1511.3
	1629.1	3040.1	3043.5	3107.8	3110.1	3127.3	3131.9	3148.9	3256.7	
<i>cjc(c2)ono</i>	99.9	114.0	172.2	188.8	219.4	267.8	326.9	330.9	372.2	453.9
	467.2	558.4	592.0	746.5	815.5	917.0	952.9	960.0	989.1	1039.8
	1152.1	1261.0	1282.6	1398.3	1414.0	1456.6	1478.8	1487.1	1496.2	1510.9
	1750.0	3035.8	3040.4	3105.7	3111.7	3115.8	3116.7	3141.8	3252.8	

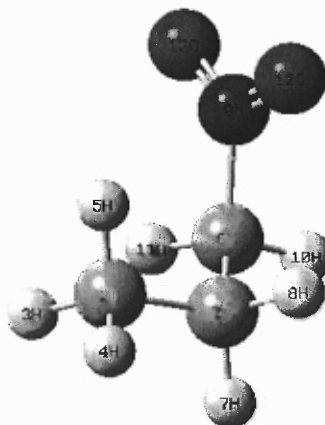


Table B1.2 Geometry Parameters of Nitro-*n*-Propane CH₃CH₂CH₂NO₂ (*ccno2*)
Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-311G(2d,d,p) Level

Bond Distances, Angstrom (Å)		Angles, degree (°)		Dihedral Angles, degree	
R(1,2)	1.531	A(2,1,3)	111.44	D(3,1,2,6)	57.91
R(1,3)	1.094	A(2,1,4)	110.60	D(3,1,2,7)	-61.83
R(1,4)	1.092	A(2,1,5)	111.20	D(3,1,2,8)	-179.66
R(1,5)	1.093	A(3,1,4)	107.77	D(4,1,2,6)	177.76
R(2,6)	1.521	A(3,1,5)	108.18	D(4,1,2,7)	58.03
R(2,7)	1.095	A(4,1,5)	107.49	D(4,1,2,8)	-59.81
R(2,8)	1.092	A(1,2,6)	113.75	D(5,1,2,6)	-62.89
R(6,9)	1.521	A(1,2,7)	110.07	D(5,1,2,7)	177.38
R(6,10)	1.092	A(1,2,8)	110.34	D(5,1,2,8)	59.54
R(6,11)	1.089	A(6,2,7)	106.75	D(1,2,6,9)	65.90
R(9,12)	1.221	A(6,2,8)	108.67	D(1,2,6,10)	-177.04
R(9,13)	1.220	A(7,2,8)	106.97	D(1,2,6,11)	-53.24
		A(2,6,9)	112.69	D(7,2,6,9)	-172.50
		A(2,6,10)	111.79	D(7,2,6,10)	-55.44
		A(2,6,11)	113.48	D(7,2,6,11)	68.36
		A(9,6,10)	104.28	D(8,2,6,9)	-57.45
		A(9,6,11)	104.97	D(8,2,6,10)	59.62
		A(10,6,11)	109.01	D(8,2,6,11)	-176.58
		A(6,9,12)	117.63	D(2,6,9,12)	36.42
		A(6,9,13)	116.81	D(2,6,9,13)	-145.42
		A(12,9,13)	125.53	D(10,6,9,12)	-85.02
				D(10,6,9,13)	93.15
				D(11,6,9,12)	160.40
				D(11,6,9,13)	-21.44

Moments of Inertia (amu unit) for *ccno2*: 277.42, 762.92 and 805.45

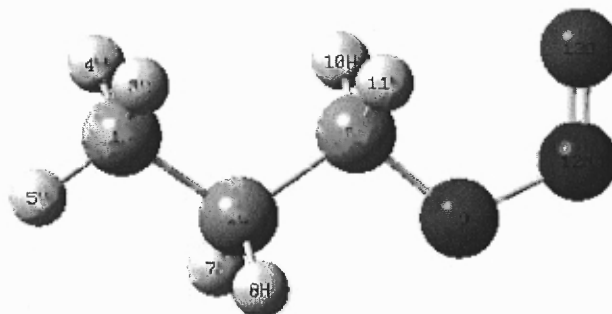


Table B1.3 Geometry Parameters of Nitrite n-propane $\text{CH}_3\text{CH}_2\text{CH}_2\text{ONO}$ (*cccono*)
Optimized at CBS-QB3 Composite, viz. B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.532	A(2,1,3)	111.45	D(3,1,2,6)	-60.20
R(1,3)	1.094	A(2,1,4)	111.45	D(3,1,2,7)	178.62
R(1,4)	1.094	A(2,1,5)	110.76	D(3,1,2,8)	60.99
R(1,5)	1.092	A(3,1,4)	107.74	D(4,1,2,6)	60.20
R(2,6)	1.520	A(3,1,5)	107.64	D(4,1,2,7)	-60.99
R(2,7)	1.094	A(4,1,5)	107.64	D(4,1,2,8)	-178.62
R(2,8)	1.094	A(1,2,6)	111.80	D(5,1,2,6)	-180.00
R(6,9)	1.448	A(1,2,7)	110.22	D(5,1,2,7)	58.81
R(6,10)	1.095	A(1,2,8)	110.22	D(5,1,2,8)	-58.81
R(6,11)	1.095	A(6,2,7)	108.83	D(1,2,6,9)	-180.00
R(9,12)	1.400	A(6,2,8)	108.83	D(1,2,6,10)	-60.54
R(12,13)	1.181	A(7,2,8)	106.79	D(1,2,6,11)	60.54
		A(2,6,9)	107.12	D(7,2,6,9)	-58.01
		A(2,6,10)	112.00	D(7,2,6,10)	61.45
		A(2,6,11)	112.00	D(7,2,6,11)	-177.47
		A(9,6,10)	109.00	D(8,2,6,9)	58.01
		A(9,6,11)	108.99	D(8,2,6,10)	177.47
		A(10,6,11)	107.67	D(8,2,6,11)	-61.44
		A(6,9,12)	116.65	D(2,6,9,12)	-180.00
		A(9,12,13)	114.78	D(10,6,9,12)	58.63
				D(11,6,9,12)	-58.63
				D(6,9,12,13)	0.02

Moments of Inertia (amu unit) for *cccono*: 144.95, 1115.54 and 1226.90

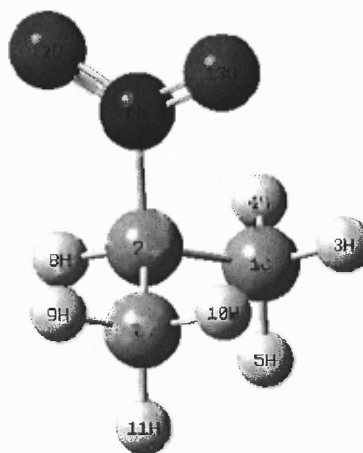


Table B1.4 Geometry Parameters of Nitro-iso-Propane $\text{CH}_3\text{CH}(\text{NO}_2)\text{CH}_3$ (*cc(no2)c*)
Optimized at CBS-QB3 Composite, viz. B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.526	A(2,1,3)	110.47	D(3,1,2,6)	62.85
R(1,3)	1.091	A(2,1,4)	111.22	D(3,1,2,7)	-57.85
R(1,4)	1.092	A(2,1,5)	109.25	D(3,1,2,8)	175.87
R(1,5)	1.092	A(3,1,4)	108.82	D(4,1,2,6)	-58.10
R(2,6)	1.529	A(3,1,5)	108.81	D(4,1,2,7)	-178.80
R(2,7)	1.525	A(4,1,5)	108.20	D(4,1,2,8)	54.92
R(2,8)	1.089	A(1,2,6)	108.41	D(5,1,2,6)	-177.48
R(6,12)	1.220	A(1,2,7)	113.62	D(5,1,2,7)	61.82
R(6,13)	1.221	A(1,2,8)	111.14	D(5,1,2,8)	-64.46
R(7,9)	1.092	A(6,2,7)	108.49	D(1,2,6,12)	117.63
R(7,10)	1.091	A(6,2,8)	103.43	D(1,2,6,13)	-62.28
R(7,11)	1.092	A(7,2,8)	111.17	D(7,2,6,12)	-118.54
		A(2,6,12)	117.37	D(7,2,6,13)	61.55
		A(2,6,13)	117.15	D(8,2,6,12)	-0.42
		A(12,6,13)	125.48	D(8,2,6,13)	179.67
		A(2,7,9)	111.23	D(1,2,7,9)	178.86
		A(2,7,10)	110.48	D(1,2,7,10)	57.91
		A(2,7,11)	109.24	D(1,2,7,11)	-61.76
		A(9,7,10)	108.80	D(6,2,7,9)	58.21
		A(9,7,11)	108.20	D(6,2,7,10)	-62.74
		A(10,7,11)	108.82	D(6,2,7,11)	177.59
				D(8,2,7,9)	-54.88
				D(8,2,7,10)	-175.83
				D(8,2,7,11)	64.50

Moments of Inertia (amu unit) for *cc(no2)c*: 351.92, 627.75 and 671.69

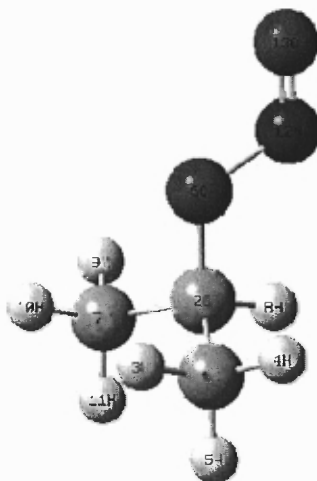


Table B1.5 Geometry Parameters of Nitrite-iso-propane $\text{CH}_3\text{CH}(\text{ONO})\text{CH}_3$ (*cc(ono)c*)
Optimized at CBS-QB3 Composite, viz. B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.524	A(2,1,3)	110.59	D(3,1,2,6)	60.44
R(1,3)	1.093	A(2,1,4)	110.63	D(3,1,2,7)	-59.51
R(1,4)	1.092	A(2,1,5)	110.34	D(3,1,2,8)	176.50
R(1,5)	1.093	A(3,1,4)	108.37	D(4,1,2,6)	-59.63
R(2,6)	1.451	A(3,1,5)	108.40	D(4,1,2,7)	-179.58
R(2,7)	1.524	A(4,1,5)	108.44	D(4,1,2,8)	56.43
R(2,8)	1.095	A(1,2,6)	108.06	D(5,1,2,6)	-179.62
R(6,12)	1.427	A(1,2,7)	113.77	D(5,1,2,7)	60.43
R(7,9)	1.092	A(1,2,8)	110.03	D(5,1,2,8)	-63.57
R(7,10)	1.093	A(6,2,7)	108.03	D(1,2,6,12)	117.98
R(7,11)	1.093	A(6,2,8)	106.63	D(7,2,6,12)	-118.52
R(12,13)	1.170	A(7,2,8)	110.04	D(8,2,6,12)	-0.28
		A(2,6,12)	111.03	D(1,2,7,9)	179.57
		A(2,7,9)	110.63	D(1,2,7,10)	59.50
		A(2,7,10)	110.60	D(1,2,7,11)	-60.43
		A(2,7,11)	110.34	D(6,2,7,9)	59.60
		A(9,7,10)	108.36	D(6,2,7,10)	-60.47
		A(9,7,11)	108.44	D(6,2,7,11)	179.60
		A(10,7,11)	108.40	D(8,2,7,9)	-56.44
		A(6,12,13)	111.23	D(8,2,7,10)	-176.51
				D(8,2,7,11)	63.56
				D(2,6,12,13)	-179.97

Moments of Inertia (amu unit) for *cc(ono)c*: 242.06, 861.77 and 1015.70

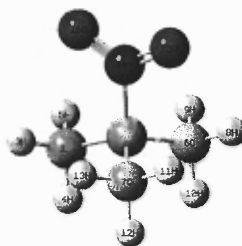


Table B1.6 Geometry Parameters of Nitro tertiary butane $\text{CH}_3\text{C}(\text{CH}_3)_2(\text{NO}_2)$
(*cc(c2)no2*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-311G(2d,d,p)
Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.525	A(2,1,3)	111.46	D(3,1,2,6)	-177.34
R(1,3)	1.09	A(2,1,4)	108.59	D(3,1,2,7)	56.47
R(1,4)	1.093	A(2,1,5)	111.46	D(3,1,2,14)	-60.44
R(1,5)	1.09	A(3,1,4)	108.58	D(4,1,2,6)	63.1
R(2,6)	1.533	A(3,1,5)	108.1	D(4,1,2,7)	-63.09
R(2,7)	1.533	A(4,1,5)	108.58	D(4,1,2,14)	-180
R(2,14)	1.557	A(1,2,6)	112	D(5,1,2,6)	-56.47
R(6,8)	1.09	A(1,2,7)	112	D(5,1,2,7)	177.34
R(6,9)	1.093	A(1,2,14)	108.89	D(5,1,2,14)	60.44
R(6,10)	1.092	A(6,2,7)	111.55	D(1,2,6,8)	176.99
R(7,11)	1.09	A(6,2,14)	106	D(1,2,6,9)	56.01
R(7,12)	1.092	A(7,2,14)	106.01	D(1,2,6,10)	-63.17
R(7,13)	1.093	A(2,6,8)	110.75	D(7,2,6,8)	-56.57
R(14,15)	1.222	A(2,6,9)	111.05	D(7,2,6,9)	-177.55
R(14,16)	1.219	A(2,6,10)	109.15	D(7,2,6,10)	63.27
		A(8,6,9)	108.78	D(14,2,6,8)	58.36
		A(8,6,10)	108.86	D(14,2,6,9)	-62.61
		A(9,6,10)	108.19	D(14,2,6,10)	178.2
		A(2,7,11)	110.75	D(1,2,7,11)	-176.98
		A(2,7,12)	109.15	D(1,2,7,12)	63.17
		A(2,7,13)	111.05	D(1,2,7,13)	-56.01
		A(11,7,12)	108.87	D(6,2,7,11)	56.58
		A(11,7,13)	108.78	D(6,2,7,12)	-63.26
		A(12,7,13)	108.19	D(6,2,7,13)	177.55
		A(2,14,15)	116.5	D(14,2,7,11)	-58.36
		A(2,14,16)	118.59	D(14,2,7,12)	-178.2
		A(15,14,16)	124.9	D(14,2,7,13)	62.62
				D(1,2,14,15)	179.99
				D(1,2,14,16)	-0.01
				D(6,2,14,15)	-59.35
				D(6,2,14,16)	120.65
				D(7,2,14,15)	59.32
				D(7,2,14,16)	-120.68

Moments of Inertia (amu unit) for *cc(c2)no2*: 535.32, 725.51 and 859.10

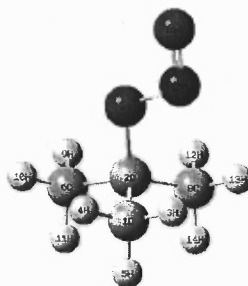


Table B1.7 Geometry Parameters of Nitrite tertiary butane $\text{CH}_3\text{C}(\text{CH}_3)_2(\text{ONO})$
 (*cc(c2)ono*) Optimized at CBS-QB3 Composite, viz. B3LYP/6-311G(2d,d,p)
 Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.531	A(2,1,3)	111.12	D(3,1,2,6)	-177.80
R(1,3)	1.091	A(2,1,4)	110.33	D(3,1,2,7)	-64.82
R(1,4)	1.093	A(2,1,5)	110.09	D(3,1,2,8)	56.77
R(1,5)	1.093	A(3,1,4)	108.58	D(4,1,2,6)	-57.32
R(2,6)	1.528	A(3,1,5)	108.31	D(4,1,2,7)	55.67
R(2,7)	1.472	A(4,1,5)	108.34	D(4,1,2,8)	177.26
R(2,8)	1.531	A(1,2,6)	111.30	D(5,1,2,6)	62.21
R(6,9)	1.092	A(1,2,7)	109.41	D(5,1,2,7)	175.19
R(6,10)	1.092	A(1,2,8)	112.15	D(5,1,2,8)	-63.22
R(6,11)	1.093	A(6,2,7)	102.85	D(1,2,6,9)	177.07
R(7,15)	1.416	A(6,2,8)	111.30	D(1,2,6,10)	57.05
R(8,12)	1.093	A(7,2,8)	109.41	D(1,2,6,11)	-62.94
R(8,13)	1.091	A(2,6,9)	110.55	D(7,2,6,9)	60.02
R(8,14)	1.093	A(2,6,10)	110.55	D(7,2,6,10)	-60.00
R(15,16)	1.174	A(2,6,11)	110.06	D(7,2,6,11)	-179.99
		A(9,6,10)	108.39	D(8,2,6,9)	-57.03
		A(9,6,11)	108.62	D(8,2,6,10)	-177.05
		A(10,6,11)	108.62	D(8,2,6,11)	62.96
		A(2,7,15)	112.60	D(1,2,7,15)	61.62
		A(2,8,12)	110.33	D(6,2,7,15)	-180.00
		A(2,8,13)	111.12	D(8,2,7,15)	-61.61
		A(2,8,14)	110.09	D(1,2,8,12)	-177.21
		A(12,8,13)	108.58	D(1,2,8,13)	-56.72
		A(12,8,14)	108.34	D(1,2,8,14)	63.27
		A(13,8,14)	108.31	D(6,2,8,12)	57.37
		A(7,15,16)	110.73	D(6,2,8,13)	177.85
				D(6,2,8,14)	-62.16
				D(7,2,8,12)	-55.62
				D(7,2,8,13)	64.87
				D(7,2,8,14)	-175.14
				D(2,7,15,16)	180.00

Moments of Inertia (amu unit) for *cc(c2)ono*: 412.35, 1052.39 and 1060.89

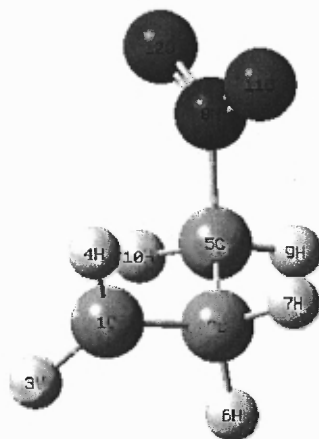


Table B1.8 Geometry Parameters of $\text{CH}_2\text{CH}_2\text{CH}_2\text{NO}_2$ (*cjcno2*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.491	A(2,1,3)	121.07	D(3,1,2,5)	92.51
R(1,3)	1.083	A(2,1,4)	120.33	D(3,1,2,6)	-27.08
R(1,4)	1.082	A(3,1,4)	118.42	D(3,1,2,7)	-146.10
R(2,5)	1.535	A(1,2,5)	113.97	D(4,1,2,5)	-82.52
R(2,6)	1.095	A(1,2,6)	110.63	D(4,1,2,6)	157.89
R(2,7)	1.093	A(1,2,7)	110.56	D(4,1,2,7)	38.87
R(5,8)	1.519	A(5,2,6)	106.20	D(1,2,5,8)	65.15
R(5,9)	1.093	A(5,2,7)	107.63	D(1,2,5,9)	-177.86
R(5,10)	1.088	A(6,2,7)	107.54	D(1,2,5,10)	-54.02
R(8,11)	1.221	A(2,5,8)	112.45	D(6,2,5,8)	-172.79
R(8,12)	1.219	A(2,5,9)	111.46	D(6,2,5,9)	-55.80
		A(2,5,10)	113.41	D(6,2,5,10)	68.04
		A(8,5,9)	104.52	D(7,2,5,8)	-57.85
		A(8,5,10)	105.17	D(7,2,5,9)	59.14
		A(9,5,10)	109.28	D(7,2,5,10)	-177.02
		A(5,8,11)	117.76	D(2,5,8,11)	32.34
		A(5,8,12)	116.60	D(2,5,8,12)	-149.60
		A(11,8,12)	125.60	D(9,5,8,11)	-88.72
				D(9,5,8,12)	89.35
				D(10,5,8,11)	156.22
				D(10,5,8,12)	-25.72

Moments of Inertia (amu unit) for *cjcno2*: 265.97, 731.45 and 789.86

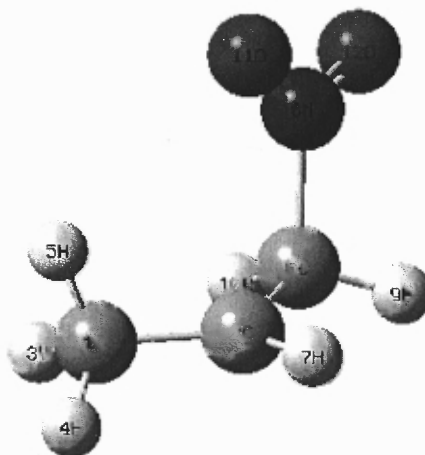


Table B1.9 Geometry Parameters of $\text{CH}_3\text{CHCH}_2\text{NO}_2$ (*ccjcn02*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.487	A(2,1,3)	111.82	D(3,1,2,6)	32.93
R(1,3)	1.095	A(2,1,4)	111.72	D(3,1,2,7)	-158.99
R(1,4)	1.093	A(2,1,5)	110.64	D(4,1,2,6)	154.77
R(1,5)	1.100	A(3,1,4)	108.52	D(4,1,2,7)	-37.15
R(2,6)	1.471	A(3,1,5)	106.84	D(5,1,2,6)	-86.04
R(2,7)	1.084	A(4,1,5)	107.07	D(5,1,2,7)	82.04
R(6,8)	1.569	A(1,2,6)	122.24	D(1,2,6,8)	80.69
R(6,9)	1.090	A(1,2,7)	118.96	D(1,2,6,9)	-161.59
R(6,10)	1.093	A(6,2,7)	117.76	D(1,2,6,10)	-35.93
R(8,11)	1.218	A(2,6,8)	113.56	D(7,2,6,8)	-87.53
R(8,12)	1.217	A(2,6,9)	114.22	D(7,2,6,9)	30.20
		A(2,6,10)	113.62	D(7,2,6,10)	155.86
		A(8,6,9)	103.00	D(2,6,8,11)	-7.18
		A(8,6,10)	102.48	D(2,6,8,12)	173.51
		A(9,6,10)	108.83	D(9,6,8,11)	-131.23
		A(6,8,11)	118.12	D(9,6,8,12)	49.46
		A(6,8,12)	115.73	D(10,6,8,11)	115.79
		A(11,8,12)	126.14	D(10,6,8,12)	-63.52

Moments of Inertia (amu unit) for *ccjcn02*: 221.45, 790.29 and 919.78

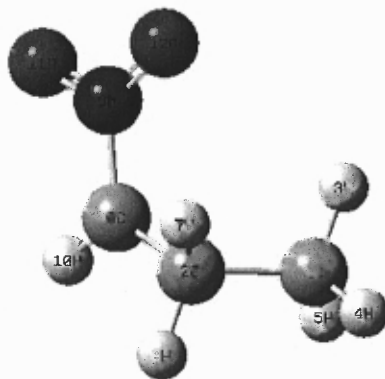


Table B1.10 Geometry Parameters of $\text{CH}_3\text{CH}_2\text{CHNO}_2$ (*cccjno2*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.551	A(2,1,3)	110.00	D(3,1,2,6)	60.78
R(1,3)	1.092	A(2,1,4)	109.59	D(3,1,2,7)	-59.74
R(1,4)	1.094	A(2,1,5)	111.33	D(3,1,2,8)	-178.28
R(1,5)	1.094	A(3,1,4)	108.63	D(4,1,2,6)	-179.85
R(2,6)	1.479	A(3,1,5)	108.90	D(4,1,2,7)	59.63
R(2,7)	1.095	A(4,1,5)	108.32	D(4,1,2,8)	-58.91
R(2,8)	1.095	A(1,2,6)	112.80	D(5,1,2,6)	-60.04
R(6,9)	1.415	A(1,2,7)	108.55	D(5,1,2,7)	179.44
R(6,10)	1.083	A(1,2,8)	109.78	D(5,1,2,8)	60.91
R(9,11)	1.244	A(6,2,7)	108.70	D(1,2,6,9)	-79.15
R(9,12)	1.243	A(6,2,8)	108.35	D(1,2,6,10)	96.83
		A(7,2,8)	108.57	D(7,2,6,9)	41.29
		A(2,6,9)	120.73	D(7,2,6,10)	-142.73
		A(2,6,10)	125.80	D(8,2,6,9)	159.10
		A(9,6,10)	113.36	D(8,2,6,10)	-24.92
		A(6,9,11)	116.76	D(2,6,9,11)	-179.92
		A(6,9,12)	118.33	D(2,6,9,12)	-0.03
		A(11,9,12)	124.90	D(10,6,9,11)	3.63
				D(10,6,9,12)	-176.47

Moments of Inertia (amu unit) for *cccjno2*: 225.68, 780.24 and 884.04

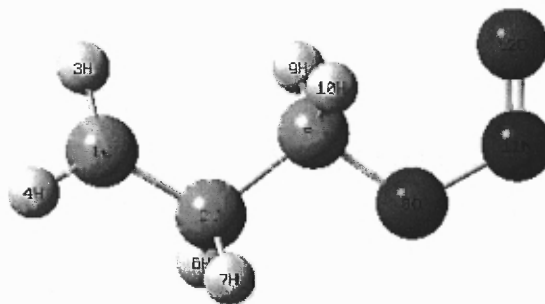


Table B1.11 Geometry Parameters of CH₂CH₂CH₂ONO (*cjccono*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.490	A(2,1,3)	120.78	D(3,1,2,5)	37.87
R(1,3)	1.084	A(2,1,4)	120.78	D(3,1,2,6)	-82.67
R(1,4)	1.082	A(3,1,4)	117.84	D(3,1,2,7)	160.40
R(2,5)	1.525	A(1,2,5)	112.28	D(4,1,2,5)	-151.22
R(2,6)	1.103	A(1,2,6)	110.68	D(4,1,2,6)	88.24
R(2,7)	1.094	A(1,2,7)	110.74	D(4,1,2,7)	-28.69
R(5,8)	1.446	A(5,2,6)	107.82	D(1,2,5,8)	-177.30
R(5,9)	1.095	A(5,2,7)	109.33	D(1,2,5,9)	-57.98
R(5,10)	1.094	A(6,2,7)	105.73	D(1,2,5,10)	63.09
R(8,11)	1.402	A(2,5,8)	106.84	D(6,2,5,8)	-55.12
R(11,12)	1.181	A(2,5,9)	111.73	D(6,2,5,9)	64.21
		A(2,5,10)	111.86	D(6,2,5,10)	-174.72
		A(8,5,9)	109.16	D(7,2,5,8)	59.38
		A(8,5,10)	109.33	D(7,2,5,9)	178.70
		A(9,5,10)	107.88	D(7,2,5,10)	-60.23
		A(5,8,11)	116.59	D(2,5,8,11)	179.48
		A(8,11,12)	114.75	D(9,5,8,11)	58.50
				D(10,5,8,11)	-59.30
				D(5,8,11,12)	-0.15

Moments of Inertia (amu unit) for *cjccono*: 137.15, 1075.56 and 1186.49

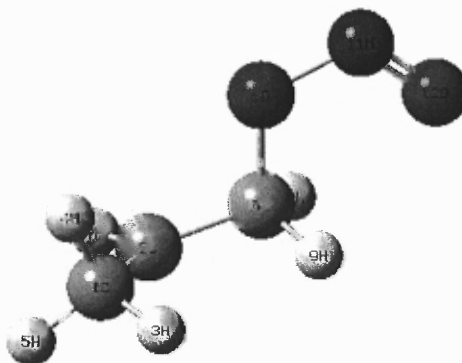


Table B1.12 Geometry Parameters of CH₃CHCH₂ONO (*ccjcono*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.4883	A(2,1,3)	111.631	D(3,1,2,6)	-37.3997
R(1,3)	1.0952	A(2,1,4)	111.2531	D(3,1,2,7)	156.1585
R(1,4)	1.1012	A(2,1,5)	111.7741	D(4,1,2,6)	81.3944
R(1,5)	1.093	A(3,1,4)	106.4792	D(4,1,2,7)	-85.0474
R(2,6)	1.4767	A(3,1,5)	108.5083	D(5,1,2,6)	-159.144
R(2,7)	1.0842	A(4,1,5)	106.931	D(5,1,2,7)	34.4142
R(6,8)	1.4826	A(1,2,6)	121.4692	D(1,2,6,8)	-74.1375
R(6,9)	1.0948	A(1,2,7)	119.1503	D(1,2,6,9)	43.6126
R(6,10)	1.092	A(6,2,7)	118.0244	D(1,2,6,10)	167.0221
R(8,11)	1.3911	A(2,6,8)	107.5043	D(7,2,6,8)	92.4514
R(11,12)	1.1828	A(2,6,9)	112.6325	D(7,2,6,9)	-149.7985
		A(2,6,10)	113.0381	D(7,2,6,10)	-26.3889
		A(8,6,9)	107.1045	D(2,6,8,11)	176.8346
		A(8,6,10)	107.7964	D(9,6,8,11)	55.5542
		A(9,6,10)	108.4869	D(10,6,8,11)	-61.0109
		A(6,8,11)	116.5422	D(6,8,11,12)	0.604
		A(8,11,12)	115.1873		

Moments of Inertia (amu unit) for *ccjcono*: 155.99, 1030.21 and 1076.89

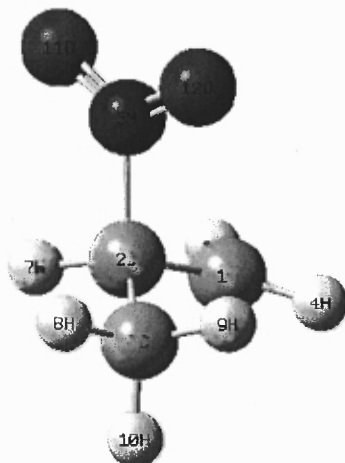


Table B1.13 Geometry Parameters of $\text{CH}_2\text{CH}(\text{NO}_2)\text{CH}_3$ (*cjc(no2)c*) Optimized at CBS-QB3 Composite, viz. B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.479	A(2,1,3)	120.40	D(3,1,2,5)	-79.25
R(1,3)	1.082	A(2,1,4)	119.97	D(3,1,2,6)	159.67
R(1,4)	1.083	A(3,1,4)	118.99	D(3,1,2,7)	30.99
R(2,5)	1.576	A(1,2,5)	107.38	D(4,1,2,5)	91.44
R(2,6)	1.521	A(1,2,6)	114.58	D(4,1,2,6)	-29.64
R(2,7)	1.090	A(1,2,7)	111.17	D(4,1,2,7)	-158.32
R(5,11)	1.218	A(5,2,6)	108.89	D(1,2,5,11)	92.38
R(5,12)	1.218	A(5,2,7)	101.54	D(1,2,5,12)	-85.45
R(6,8)	1.092	A(6,2,7)	112.32	D(6,2,5,11)	-143.03
R(6,9)	1.090	A(2,5,11)	116.25	D(6,2,5,12)	39.15
R(6,10)	1.092	A(2,5,12)	117.59	D(7,2,5,11)	-24.38
		A(11,5,12)	126.12	D(7,2,5,12)	157.80
		A(2,6,8)	111.29	D(1,2,6,8)	178.32
		A(2,6,9)	110.43	D(1,2,6,9)	57.71
		A(2,6,10)	109.07	D(1,2,6,10)	-62.04
		A(8,6,9)	108.53	D(5,2,6,8)	58.07
		A(8,6,10)	108.47	D(5,2,6,9)	-62.53
		A(9,6,10)	108.99	D(5,2,6,10)	177.72
				D(7,2,6,8)	-53.58
				D(7,2,6,9)	-174.18
				D(7,2,6,10)	66.07

Moments of Inertia (amu unit) for *cjc(no2)c*: 341.80, 579.54 and 701.28

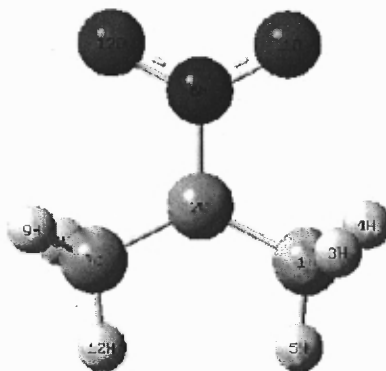


Table B1.14 Geometry Parameters of $\text{CH}_3\text{C}(\text{NO}_2)\text{CH}_3$ (*ccj(no2)c*) Optimized at CBS-QB3 Composite, viz. B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.482	A(2,1,3)	110.80	D(3,1,2,6)	67.72
R(1,3)	1.098	A(2,1,4)	110.92	D(3,1,2,7)	-112.30
R(1,4)	1.094	A(2,1,5)	110.68	D(4,1,2,6)	-49.26
R(1,5)	1.090	A(3,1,4)	105.63	D(4,1,2,7)	130.72
R(2,6)	1.425	A(3,1,5)	108.78	D(5,1,2,6)	-171.52
R(2,7)	1.482	A(4,1,5)	109.90	D(5,1,2,7)	8.47
R(6,11)	1.239	A(1,2,6)	117.12	D(1,2,6,11)	-1.89
R(6,12)	1.239	A(1,2,7)	125.77	D(1,2,6,12)	178.06
R(7,8)	1.098	A(6,2,7)	117.12	D(7,2,6,11)	178.12
R(7,9)	1.094	A(2,6,11)	117.74	D(7,2,6,12)	-1.93
R(7,10)	1.090	A(2,6,12)	117.74	D(1,2,7,8)	-112.22
		A(11,6,12)	124.52	D(1,2,7,9)	130.79
		A(2,7,8)	110.80	D(1,2,7,10)	8.53
		A(2,7,9)	110.92	D(6,2,7,8)	67.76
		A(2,7,10)	110.68	D(6,2,7,9)	-49.22
		A(8,7,9)	105.63	D(6,2,7,10)	-171.48
		A(8,7,10)	108.78		
		A(9,7,10)	109.90		

Moments of Inertia (amu unit) for *ccj(no2)c*: 360.26, 474.38 and 812.54

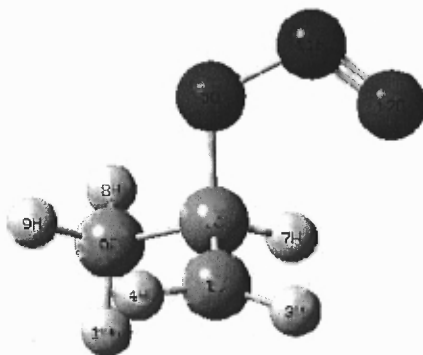


Table B1.15 Geometry Parameters of $\text{CH}_2\text{CH}(\text{ONO})\text{CH}_3$ (*cjc(ono)c*) Optimized at CBS-QB3 Composite, viz. B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.4813	A(2,1,3)	120.9464	D(3,1,2,5)	-93.664
R(1,3)	1.0812	A(2,1,4)	119.6082	D(3,1,2,6)	149.7985
R(1,4)	1.0836	A(3,1,4)	118.9289	D(3,1,2,7)	23.2181
R(2,5)	1.4971	A(1,2,5)	110.1413	D(4,1,2,5)	78.0044
R(2,6)	1.5219	A(1,2,6)	114.3847	D(4,1,2,6)	-38.5331
R(2,7)	1.0919	A(1,2,7)	110.5628	D(4,1,2,7)	-165.1135
R(5,11)	1.3855	A(5,2,6)	103.8794	D(1,2,5,11)	78.0281
R(6,8)	1.0915	A(5,2,7)	106.0524	D(6,2,5,11)	-159.0425
R(6,9)	1.0923	A(6,2,7)	111.2965	D(7,2,5,11)	-41.63
R(6,10)	1.0926	A(2,5,11)	117.6905	D(1,2,6,8)	176.7162
R(11,12)	1.184	A(2,6,8)	110.5604	D(1,2,6,9)	56.4484
		A(2,6,9)	110.6746	D(1,2,6,10)	-63.2994
		A(2,6,10)	109.7892	D(5,2,6,8)	56.6209
		A(8,6,9)	108.5149	D(5,2,6,9)	-63.6469
		A(8,6,10)	108.7474	D(5,2,6,10)	176.6053
		A(9,6,10)	108.4986	D(7,2,6,8)	-57.0841
		A(5,11,12)	115.6542	D(7,2,6,9)	-177.352
				D(7,2,6,10)	62.9003
				D(2,5,11,12)	-1.8574

Moments of Inertia (amu unit) for *cjc(ono)c*: 262.68, 681.68 and 826.46

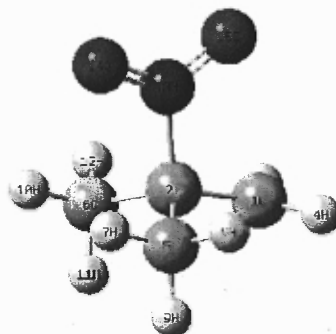


Table B1.16 Geometry Parameters of $\text{CH}_2\text{C}(\text{CH}_3)_2(\text{NO}_2)$ (*cjc(c2)no2*) Optimized at CBS-QB3 Composite, viz. B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.480	A(2,1,3)	120.42	D(3,1,2,5)	159.05
R(1,3)	1.082	A(2,1,4)	120.42	D(3,1,2,6)	30.80
R(1,4)	1.082	A(3,1,4)	118.45	D(3,1,2,13)	-85.07
R(2,5)	1.532	A(1,2,5)	112.78	D(4,1,2,5)	-30.79
R(2,6)	1.532	A(1,2,6)	112.78	D(4,1,2,6)	-159.03
R(2,13)	1.597	A(1,2,13)	108.02	D(4,1,2,13)	85.09
R(5,7)	1.090	A(5,2,6)	112.10	D(1,2,5,7)	174.76
R(5,8)	1.093	A(5,2,13)	105.24	D(1,2,5,8)	53.88
R(5,9)	1.092	A(6,2,13)	105.24	D(1,2,5,9)	-65.39
R(6,10)	1.090	A(2,5,7)	110.57	D(6,2,5,7)	-56.65
R(6,11)	1.092	A(2,5,8)	110.99	D(6,2,5,8)	-177.53
R(6,12)	1.093	A(2,5,9)	109.13	D(6,2,5,9)	63.21
R(13,14)	1.218	A(7,5,8)	108.83	D(13,2,5,7)	57.23
R(13,15)	1.218	A(7,5,9)	108.97	D(13,2,5,8)	-63.65
		A(8,5,9)	108.29	D(13,2,5,9)	177.08
		A(2,6,10)	110.57	D(1,2,6,10)	-174.76
		A(2,6,11)	109.13	D(1,2,6,11)	65.39
		A(2,6,12)	110.99	D(1,2,6,12)	-53.87
		A(10,6,11)	108.97	D(5,2,6,10)	56.65
		A(10,6,12)	108.83	D(5,2,6,11)	-63.20
		A(11,6,12)	108.29	D(5,2,6,12)	177.53
		A(2,13,14)	116.92	D(13,2,6,10)	-57.22
		A(2,13,15)	117.68	D(13,2,6,11)	-177.08
		A(14,13,15)	125.39	D(13,2,6,12)	63.66
				D(1,2,13,14)	180.00
				D(1,2,13,15)	0.00
				D(5,2,13,14)	-59.29
				D(5,2,13,15)	120.70
				D(6,2,13,14)	59.29
				D(6,2,13,15)	-120.71

Moments of Inertia (amu unit) for *cjc(c2)no2*: 524.42, 721.02 and 840.56

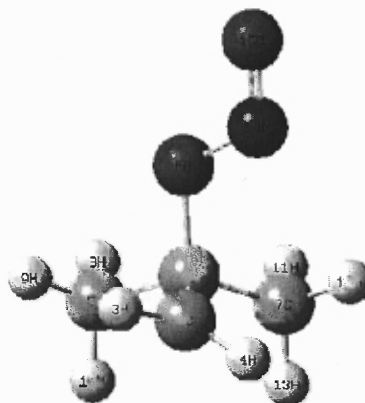


Table B1.17 Geometry Parameters of $\text{CH}_2\text{C}(\text{CH}_3)_2(\text{ONO})$ (*cjc(c2)ono*) Optimized at CBS-QB3 Composite, viz. B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.490	A(2,1,3)	119.47	D(3,1,2,5)	-50.47
R(1,3)	1.083	A(2,1,4)	121.47	D(3,1,2,6)	61.93
R(1,4)	1.082	A(3,1,4)	118.88	D(3,1,2,7)	-176.97
R(2,5)	1.533	A(1,2,5)	111.46	D(4,1,2,5)	134.47
R(2,6)	1.489	A(1,2,6)	109.71	D(4,1,2,6)	-113.13
R(2,7)	1.529	A(1,2,7)	112.61	D(4,1,2,7)	7.97
R(5,8)	1.092	A(5,2,6)	102.14	D(1,2,5,8)	174.87
R(5,9)	1.092	A(5,2,7)	111.74	D(1,2,5,9)	55.03
R(5,10)	1.092	A(6,2,7)	108.62	D(1,2,5,10)	-65.00
R(6,14)	1.417	A(2,5,8)	110.20	D(6,2,5,8)	57.79
R(7,11)	1.092	A(2,5,9)	110.44	D(6,2,5,9)	-62.06
R(7,12)	1.092	A(2,5,10)	110.02	D(6,2,5,10)	177.91
R(7,13)	1.093	A(8,5,9)	108.49	D(7,2,5,8)	-58.15
R(14,15)	1.173	A(8,5,10)	108.93	D(7,2,5,9)	-177.99
		A(9,5,10)	108.73	D(7,2,5,10)	61.98
		A(2,6,14)	111.34	D(1,2,6,14)	54.40
		A(2,7,11)	110.33	D(5,2,6,14)	172.74
		A(2,7,12)	110.65	D(7,2,6,14)	-69.08
		A(2,7,13)	110.13	D(1,2,7,11)	-177.21
		A(11,7,12)	108.64	D(1,2,7,12)	-56.95
		A(11,7,13)	108.57	D(1,2,7,13)	62.96
		A(12,7,13)	108.46	D(5,2,7,11)	56.44
		A(6,14,15)	110.74	D(5,2,7,12)	176.69
				D(5,2,7,13)	-63.40
				D(6,2,7,11)	-55.48
				D(6,2,7,12)	64.78
				D(6,2,7,13)	-175.32
				D(2,6,14,15)	179.98

Moments of Inertia (amu unit) for *cjc(c2)ono*: 399.76, 1029.02 and 1048.07

APPENDIX C

VIBRATION FREQUENCIES AND OPTIMIZED GEOMETRY OF NITROCARBONYLS, NITROOLEFINS, CORRESPONDING NITRITES AND THEIR CARBON CENTERED RADICALS

Table C2.1 Calculated at CBS-QB3 composite, viz. B3LYP/6-311G(2d,d,p) Level
Vibration Frequencies

System	Frequencies, cm ⁻¹									
<i>cc(=o)cno2</i>	21.5	42	159.2	178.8	365	455.2	472.3	489.9	644.7	754.9
	799.4	870.7	933.7	1010.1	1073.6	1203.8	1215.4	1302.9	1389.6	1412.1
	1439.3	1466.2	1471.1	1636.3	1816.4	3037.4	3095.4	3099.3	3154	3171.8
<i>cjc(=o)cno2</i>	17.7	54.3	206.1	365.6	401.6	455	477.8	530.3	641.8	754.5
	802.2	862.2	932.3	963.4	1043.3	1196.7	1268.2	1310	1410.1	1454.2
	1463	1561.7	1639.1	3092.5	3158.5	3184.2	3278.2			
<i>cc(=o)cjno2</i>	55.2	104.5	136.1	213.5	361.1	407	497.8	535.9	627.3	725.7
	764.5	828.1	999.1	1023.8	1033.6	1235.1	1310.2	1345.1	1400.3	1456.2
	1470.3	1542.7	1630.6	3051.1	3113.4	3149.2	3238.3			
<i>cc(=o)cono</i>	47.7	58.7	152.7	174.1	261.5	334.8	402.3	475.1	512.2	627.2
	757.5	802.8	886.3	992.3	1072.4	1104.5	1230	1274.7	1354.2	1386.9
	1448.5	1460.9	1468.6	1796.9	1809.1	3029.1	3035.1	3092	3101.3	3148.8
<i>cjc(=o)cono</i>	38.9	54	206.9	341.2	354.5	408.6	467	485.6	530	576.8
	786.4	822.7	865.7	970.3	999.5	1043	1265.8	1281.4	1354.4	1442.1
	1459.8	1558	1730.7	3069.5	3122.5	3156.3	3273.5			
<i>c=cno2</i>	108.4	330.8	540.5	554	655.2	818.4	902.8	978.8	1004.1	1076.9
	1284.1	1387.4	1403	1613.4	1701.6	3162.3	3241.5	3262.4		
<i>cj=cno2</i>	90.3	282.8	554.5	566	579.3	790	796.9	837.5	949.1	1214.7
	1369.4	1618.8	1660.1	3157.2	3295.6					
<i>c=cjno2</i>	30.7	266.9	482.9	512.8	634.4	781.1	893	947.5	1048.6	1364.5
	1384.4	1596.3	1674.9	3107.3	3210.7					
<i>c=cono</i>	114.3	214.5	238.2	419.5	595.8	714.1	796.3	885.9	977.4	989.7
	1206	1324.9	1424.5	1694.8	1817.9	3156.5	3169.7	3254.6		
<i>cj=cono</i>	115.1	222	244.3	422.9	567.9	621	777.5	799.6	832.4	1140.7
	1283.8	1669.3	1822.2	3073.1	3295.5					

Table C2.1 (continued)

System	Frequencies, cm ⁻¹									
<i>cc(=o)no2</i>	40.3	130.7	278.8	371.5	409.1	469.1	604.2	667.6	844.1	969.9
	1043.3	1133.5	1383	1395.8	1455.4	1455.9	1664.2	1940.7	3057.4	3120.8
	3159.4									
<i>cjc(=o)no2</i>	37.7	302.8	349.1	392.8	449.1	476.5	603.6	712.9	831.3	849.6
	1014.6	1198.2	1382.9	1441.4	1660.7	1685.8	3173.2	3301.4		
<i>cc(=o)ono</i>	50.8	86.3	128.6	317.2	195.1	514.9	562.3	591.5	723.8	974.6
	991.5	1063.9	1205.2	1391.9	1468.9	1473.1	1831.6	1889	3049.4	3112.1
	3153.3									
<i>cjc(=o)ono</i>	31.6	130.3	201.3	319	327.5	511.4	562.7	612.7	751.1	774.8
	961	1023.8	1229.7	1447.1	1684.8	1872.6	3162.9	3285.8		

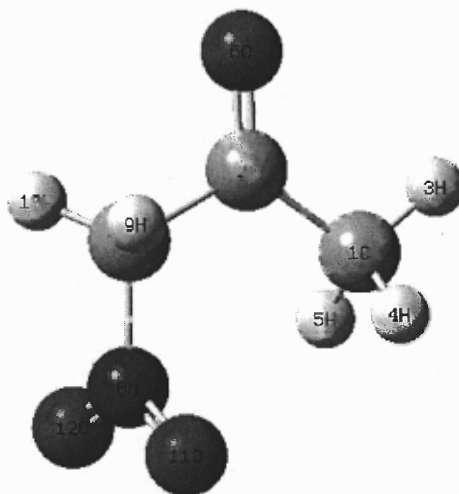


Table C2.2 Geometry Parameters of Nitroacetone $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{NO}_2$ (*cc(=o)cno2*)
Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.51	A(2,1,3)	109.24	D(3,1,2,6)	2.02
R(1,3)	1.09	A(2,1,4)	110.39	D(3,1,2,7)	-176.54
R(1,4)	1.09	A(2,1,5)	109.99	D(4,1,2,6)	123.59
R(1,5)	1.09	A(3,1,4)	110.39	D(4,1,2,7)	-54.98
R(2,6)	1.20	A(3,1,5)	109.93	D(5,1,2,6)	-118.71
R(2,7)	1.55	A(4,1,5)	106.88	D(5,1,2,7)	62.73
R(7,8)	1.50	A(1,2,6)	124.27	D(1,2,7,8)	-13.59
R(7,9)	1.09	A(1,2,7)	118.84	D(1,2,7,9)	105.44
R(7,10)	1.09	A(6,2,7)	116.88	D(1,2,7,10)	-133.46
R(8,11)	1.22	A(2,7,8)	113.59	D(6,2,7,8)	167.73
R(8,12)	1.22	A(2,7,9)	108.60	D(6,2,7,9)	-73.23
		A(2,7,10)	108.74	D(6,2,7,10)	47.86
		A(8,7,9)	107.10	D(2,7,8,11)	90.67
		A(8,7,10)	107.68	D(2,7,8,12)	-86.90
		A(9,7,10)	111.16	D(9,7,8,11)	-29.23
		A(7,8,11)	117.24	D(9,7,8,12)	153.21
		A(7,8,12)	116.89	D(10,7,8,11)	-148.86
		A(11,8,12)	125.81	D(10,7,8,12)	33.58

Moments of Inertia (amu unit) for *cc(=o)cno2*: 354.21, 1016.94 and 1090.42

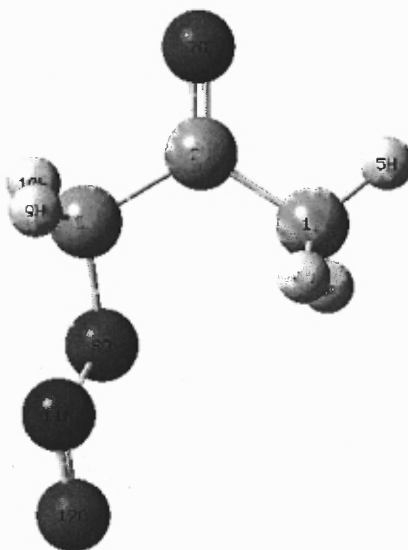


Table C2.3 Geometry Parameters of 2 Propanone nitrite $\text{CH}_3\text{C}(=\text{O})\text{CH}_2\text{ONO}$
(*cc(=o)ono*) Optimized at CBS-QB3 Composite, viz. B3LYP/6-311G(2d,d,p)
Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.51	A(2,1,3)	110.17	D(3,1,2,6)	59.60
R(1,3)	1.09	A(2,1,4)	110.41	D(3,1,2,7)	-121.50
R(1,4)	1.09	A(2,1,5)	109.35	D(4,1,2,6)	-57.68
R(1,5)	1.09	A(3,1,4)	106.44	D(4,1,2,7)	121.22
R(2,6)	1.53	A(3,1,5)	110.48	D(5,1,2,6)	-178.79
R(2,7)	1.21	A(4,1,5)	109.96	D(5,1,2,7)	0.11
R(6,8)	1.43	A(1,2,6)	117.87	D(1,2,6,8)	-17.03
R(6,9)	1.10	A(1,2,7)	123.70	D(1,2,6,9)	104.26
R(6,10)	1.09	A(6,2,7)	118.42	D(1,2,6,10)	-138.17
R(8,11)	1.45	A(2,6,8)	113.32	D(7,2,6,8)	164.01
R(11,12)	1.16	A(2,6,9)	108.08	D(7,2,6,9)	-74.70
		A(2,6,10)	108.67	D(7,2,6,10)	42.87
		A(8,6,9)	109.30	D(2,6,8,11)	114.64
		A(8,6,10)	108.85	D(9,6,8,11)	-5.97
		A(9,6,10)	108.50	D(10,6,8,11)	-124.32
		A(6,8,11)	110.55	D(6,8,11,12)	-179.03
		A(8,11,12)	111.02		

Moments of Inertia (amu unit) for *cc(=o)ono*: 254.56, 1311.02 and 1483.46

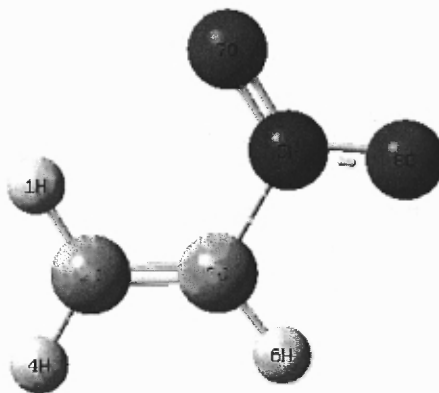


Table C2.4 Geometry Parameters of Nitroethylene $\text{CH}_2=\text{CHNO}_2$ ($c=cno2$) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.08	A(1,2,3)	120.45	D(1,2,3,5)	0.00
R(2,3)	1.32	A(1,2,4)	119.21	D(1,2,3,6)	180.00
R(2,4)	1.08	A(3,2,4)	120.34	D(4,2,3,5)	180.00
R(3,5)	1.47	A(2,3,5)	120.84	D(4,2,3,6)	0.00
R(3,6)	1.08	A(2,3,6)	127.41	D(2,3,5,7)	0.00
R(5,7)	1.22	A(5,3,6)	111.76	D(2,3,5,8)	-179.99
R(5,8)	1.22	A(3,5,7)	118.92	D(6,3,5,7)	180.00
		A(3,5,8)	115.48	D(6,3,5,8)	0.01
		A(7,5,8)	125.60		

Moments of Inertia (amu unit) for $c=cno2$: 152.31, 386.03 and 538.34

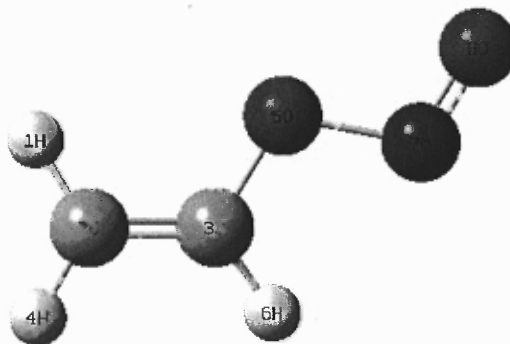


Table C2.5 Geometry Parameters of Vinyl nitrite $\text{CH}_2=\text{CHONO}$ ($c=cono$) Optimized at CBS-QB3 Composite, viz. B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.08	A(1,2,3)	121.49	D(1,2,3,5)	0.01
R(2,3)	1.33	A(1,2,4)	118.72	D(1,2,3,6)	180.00
R(2,4)	1.08	A(3,2,4)	119.79	D(4,2,3,5)	-179.99
R(3,5)	1.37	A(2,3,5)	121.56	D(4,2,3,6)	0.00
R(3,6)	1.09	A(2,3,6)	124.22	D(2,3,5,7)	-179.98
R(5,7)	1.48	A(5,3,6)	114.22	D(6,3,5,7)	0.03
R(7,8)	1.16	A(3,5,7)	110.56	D(3,5,7,8)	180.00
		A(5,7,8)	110.53		

Moments of Inertia (amu unit) for $c=cono$: 42.65, 693.49 and 736.15

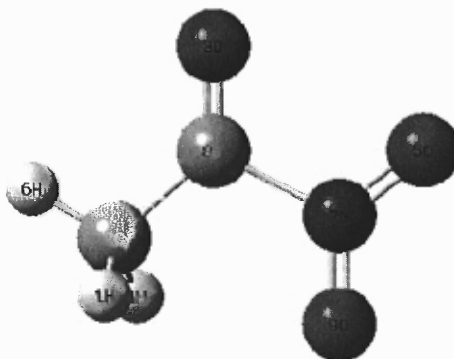


Table C2.6 Geometry Parameters of Nitroacetate $\text{CH}_3\text{C}(=\text{O})\text{NO}_2$ (*cc(=o)no2*)
Optimized at CBS-QB3 Composite, viz. B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.09	A(1,2,4)	106.60	D(1,2,8,3)	-121.36
R(2,4)	1.09	A(1,2,6)	110.79	D(1,2,8,7)	58.61
R(2,6)	1.09	A(1,2,8)	109.96	D(4,2,8,3)	121.55
R(2,8)	1.49	A(4,2,6)	110.80	D(4,2,8,7)	-58.48
R(3,8)	1.18	A(4,2,8)	109.97	D(6,2,8,3)	0.09
R(5,7)	1.21	A(6,2,8)	108.72	D(6,2,8,7)	-179.95
R(7,8)	1.61	A(5,7,8)	116.25	D(5,7,8,2)	179.90
R(7,9)	1.22	A(5,7,9)	127.46	D(5,7,8,3)	-0.13
		A(8,7,9)	116.30	D(9,7,8,2)	0.03
		A(2,8,3)	130.83	D(9,7,8,3)	-180.00
		A(2,8,7)	112.61		
		A(3,8,7)	116.56		

Moments of Inertia (amu unit) for *cc(=o)no2*: 313.64, 488.55 and 791.17

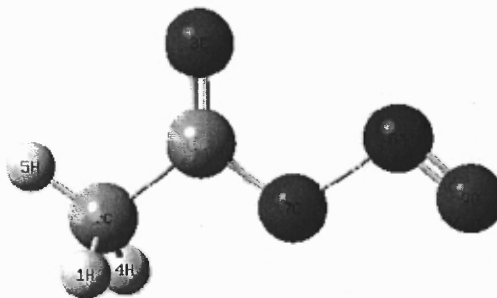


Table C2.7 Geometry Parameters of Acetyl nitrite $\text{CH}_3\text{C}(=\text{O})\text{NO}_2$ (*cc(=o)ono*)
Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.09	A(1,2,4)	107.43	D(1,2,6,3)	-120.95
R(2,4)	1.09	A(1,2,5)	110.17	D(1,2,6,7)	59.04
R(2,5)	1.09	A(1,2,6)	109.96	D(4,2,6,3)	120.95
R(2,6)	1.51	A(4,2,5)	110.17	D(4,2,6,7)	-59.05
R(3,6)	1.20	A(4,2,6)	109.96	D(5,2,6,3)	0.00
R(6,7)	1.38	A(5,2,6)	109.13	D(5,2,6,7)	180.00
R(7,8)	1.56	A(2,6,3)	126.10	D(2,6,7,8)	-180.00
R(8,9)	1.14	A(2,6,7)	109.45	D(3,6,7,8)	0.00
		A(3,6,7)	124.44	D(6,7,8,9)	-179.99
		A(6,7,8)	113.44		
		A(7,8,9)	108.33		

Moments of Inertia (amu unit) for *cc(=o)ono*: 183.21, 809.92 and 981.98

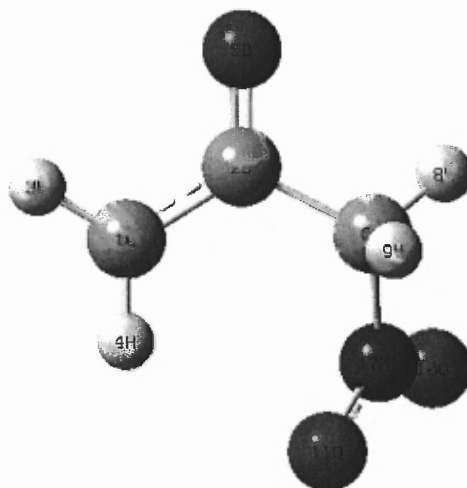


Table C2.8 Geometry Parameters of $\text{CH}_2\text{C}(=\text{O})\text{CH}_2\text{NO}_2$ (*cjc(=o)cno2*) Optimized at CBS-QB3 Composite, viz. B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.43	A(2,1,3)	117.29	D(3,1,2,5)	2.74
R(1,3)	1.08	A(2,1,4)	122.45	D(3,1,2,6)	179.92
R(1,4)	1.08	A(3,1,4)	120.26	D(4,1,2,5)	-176.22
R(2,5)	1.23	A(1,2,5)	122.36	D(4,1,2,6)	0.96
R(2,6)	1.54	A(1,2,6)	120.59	D(1,2,6,7)	37.41
R(6,7)	1.51	A(5,2,6)	116.99	D(1,2,6,8)	157.01
R(6,8)	1.09	A(2,6,7)	113.73	D(1,2,6,9)	-81.24
R(6,9)	1.09	A(2,6,8)	108.54	D(5,2,6,7)	-145.26
R(7,10)	1.22	A(2,6,9)	109.55	D(5,2,6,8)	-25.67
R(7,11)	1.22	A(7,6,8)	107.50	D(5,2,6,9)	96.09
		A(7,6,9)	106.20	D(2,6,7,10)	102.25
		A(8,6,9)	111.34	D(2,6,7,11)	-76.61
		A(6,7,10)	117.31	D(8,6,7,10)	-17.93
		A(6,7,11)	116.94	D(8,6,7,11)	163.21
		A(10,7,11)	125.74	D(9,6,7,10)	-137.20
				D(9,6,7,11)	43.94

Moments of Inertia (amu unit) for *cjc(=o)cno2*: 341.10, 960.31 and 1145.14

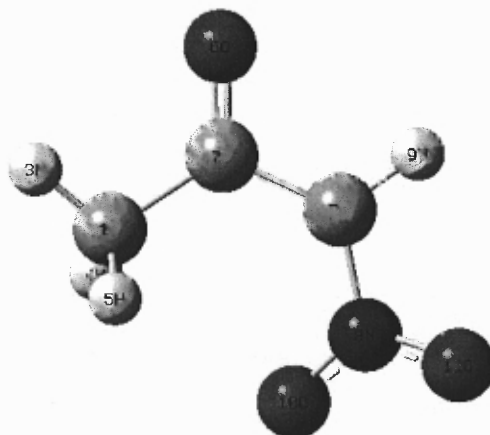


Table C2.9 Geometry Parameters of $\text{CH}_3\text{C}(=\text{O})\text{CHNO}_2$ (*cc(=o)cjno2*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.51	A(2,1,3)	108.05	D(3,1,2,6)	-12.13
R(1,3)	1.09	A(2,1,4)	109.96	D(3,1,2,7)	167.92
R(1,4)	1.09	A(2,1,5)	111.86	D(4,1,2,6)	107.77
R(1,5)	1.09	A(3,1,4)	109.86	D(4,1,2,7)	-72.17
R(2,6)	1.23	A(3,1,5)	110.46	D(5,1,2,6)	-133.93
R(2,7)	1.46	A(4,1,5)	106.65	D(5,1,2,7)	46.13
R(7,8)	1.43	A(1,2,6)	122.49	D(1,2,7,8)	3.57
R(7,9)	1.08	A(1,2,7)	122.31	D(1,2,7,9)	-174.94
R(8,10)	1.23	A(6,2,7)	115.20	D(6,2,7,8)	-176.38
R(8,11)	1.23	A(2,7,8)	125.78	D(6,2,7,9)	5.12
		A(2,7,9)	119.90	D(2,7,8,10)	28.64
		A(8,7,9)	114.31	D(2,7,8,11)	-151.35
		A(7,8,10)	118.81	D(9,7,8,10)	-152.78
		A(7,8,11)	115.74	D(9,7,8,11)	27.23
		A(10,8,11)	125.45		

Moments of Inertia (amu unit) for *cjc(=o)cno2*: 320.91, 978.55 and 1239.95

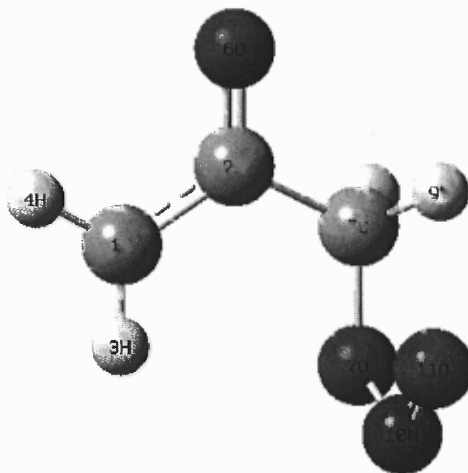


Table C2.10 Geometry Parameters of $\text{CH}_2\text{C}(=\text{O})\text{CH}_2\text{ONO}$ (*cjc(=o)cono*) Optimized at CBS-QB3 Composite, viz. B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.43	A(2,1,3)	122.07	D(3,1,2,5)	-0.99
R(1,3)	1.08	A(2,1,4)	117.92	D(3,1,2,6)	177.01
R(1,4)	1.08	A(3,1,4)	120.00	D(4,1,2,5)	-179.79
R(2,5)	1.54	A(1,2,5)	119.91	D(4,1,2,6)	-1.78
R(2,6)	1.23	A(1,2,6)	122.28	D(1,2,5,7)	-10.51
R(5,7)	1.43	A(5,2,6)	117.78	D(1,2,5,8)	106.74
R(5,8)	1.09	A(2,5,7)	114.67	D(1,2,5,9)	-134.98
R(5,9)	1.09	A(2,5,8)	108.85	D(6,2,5,7)	171.39
R(7,10)	1.44	A(2,5,9)	108.10	D(6,2,5,8)	-71.36
R(10,11)	1.17	A(7,5,8)	105.01	D(6,2,5,9)	46.92
		A(7,5,9)	111.05	D(2,5,7,10)	-88.24
		A(8,5,9)	109.02	D(8,5,7,10)	152.34
		A(5,7,10)	116.62	D(9,5,7,10)	34.65
		A(7,10,11)	114.91	D(5,7,10,11)	0.62

Moments of Inertia (amu unit) for *cjc(=o)cono*: 346.45, 1035.69 and 1068.68

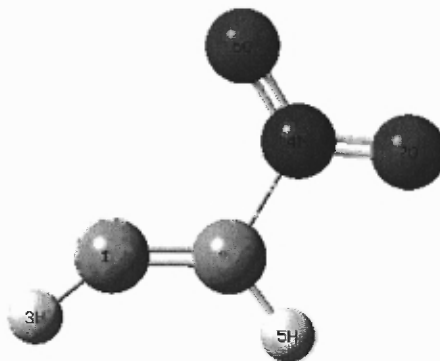


Table C2.11 Geometry Parameters of CH=CHNO₂ (*cj=cno2*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.30	A(2,1,3)	140.71	D(3,1,2,4)	-180.00
R(1,3)	1.08	A(1,2,4)	120.75	D(3,1,2,5)	0.00
R(2,4)	1.49	A(1,2,5)	127.43	D(1,2,4,6)	0.03
R(2,5)	1.09	A(4,2,5)	111.82	D(1,2,4,7)	179.97
R(4,6)	1.22	A(2,4,6)	118.33	D(5,2,4,6)	-179.97
R(4,7)	1.22	A(2,4,7)	115.48	D(5,2,4,7)	-0.03
		A(6,4,7)	126.19		

Moments of Inertia (amu unit) for *cj=cno2*: 146.87, 373.74 and 520.62

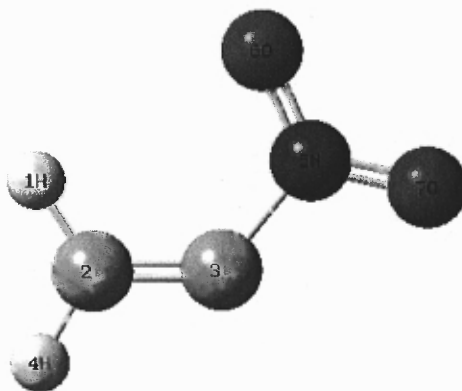


Table C2.12 Geometry Parameters of $\text{CH}_2=\text{CNO}_2$ ($c=cjno2$) Optimized at CBS-QB3 Composite, viz. B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.09	A(1,2,3)	120.88	D(1,2,3,5)	0.00
R(2,3)	1.31	A(1,2,4)	118.41	D(4,2,3,5)	180.00
R(2,4)	1.08	A(3,2,4)	120.70	D(2,3,5,6)	0.02
R(3,5)	1.44	A(2,3,5)	129.92	D(2,3,5,7)	179.99
R(5,6)	1.22	A(3,5,6)	117.48		
R(5,7)	1.22	A(3,5,7)	116.28		
		A(6,5,7)	126.24		

Moments of Inertia (amu unit) for $c=cjno2$: 140.09, 394.99 and 535.09

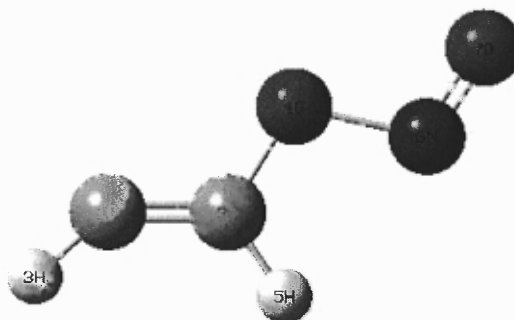


Table C2.13 Geometry Parameters of CH=CHONO (*cj=cono*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.31	A(2,1,3)	138.33	D(3,1,2,4)	-180.00
R(1,3)	1.08	A(1,2,4)	122.37	D(3,1,2,5)	0.00
R(2,4)	1.38	A(1,2,5)	123.71	D(1,2,4,6)	-180.00
R(2,5)	1.09	A(4,2,5)	113.92	D(5,2,4,6)	0.00
R(4,6)	1.48	A(2,4,6)	109.93	D(2,4,6,7)	179.99
R(6,7)	1.16	A(4,6,7)	110.49		

Moments of Inertia (amu unit) for *cj=cono*: 36.19, 671.58 and 707.77

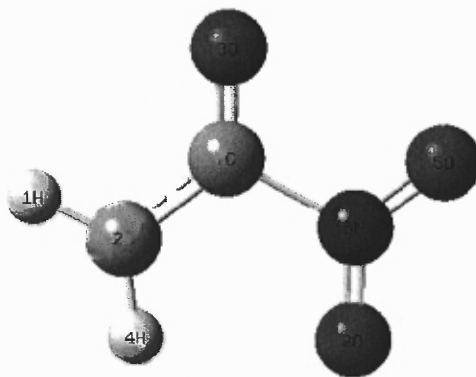


Table C2.14 Geometry Parameters of $\text{CH}_2\text{C}(=\text{O})\text{NO}_2$ (*cjc(=o)no2*) Optimized at CBS-QB3 Composite, *viz.* B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.08	A(1,2,4)	121.37	D(1,2,7,3)	0.00
R(2,4)	1.08	A(1,2,7)	117.46	D(1,2,7,6)	180.00
R(2,7)	1.42	A(4,2,7)	121.17	D(4,2,7,3)	180.00
R(3,7)	1.20	A(5,6,7)	115.90	D(4,2,7,6)	0.00
R(5,6)	1.21	A(5,6,8)	127.19	D(5,6,7,2)	179.82
R(6,7)	1.59	A(7,6,8)	116.90	D(5,6,7,3)	-0.18
R(6,8)	1.22	A(2,7,3)	129.29	D(8,6,7,2)	-0.20
		A(2,7,6)	113.89	D(8,6,7,3)	179.80
		A(3,7,6)	116.82		

Moments of Inertia (amu unit) for *cjc(=o)no2*: 296.03, 469.70 and 765.73

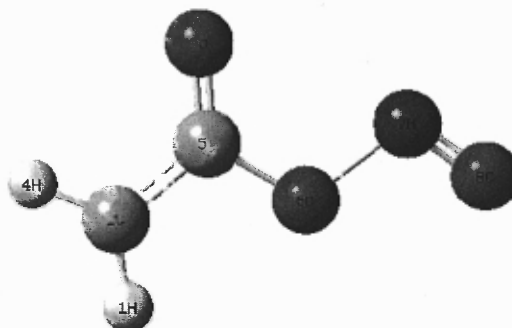


Table C2.15 Geometry Parameters of $\text{CH}_2\text{C}(=\text{O})\text{ONO}$ (*cjc(=o)ono*) Optimized at CBS-QB3 Composite, viz. B3LYP/6-311G(2d,d,p) Level

Bond Distances, angstrom		Angles, degree		Dihedral Angles, degree	
R(1,2)	1.08	A(1,2,4)	120.85	D(1,2,5,3)	-179.18
R(2,4)	1.08	A(1,2,5)	121.36	D(1,2,5,6)	1.54
R(2,5)	1.44	A(4,2,5)	117.79	D(4,2,5,3)	1.16
R(3,5)	1.21	A(2,5,3)	124.95	D(4,2,5,6)	-178.12
R(5,6)	1.38	A(2,5,6)	110.87	D(2,5,6,7)	-170.80
R(6,7)	1.55	A(3,5,6)	124.18	D(3,5,6,7)	9.91
R(7,8)	1.15	A(5,6,7)	112.99	D(5,6,7,8)	-176.34
		A(6,7,8)	108.56		

Moments of Inertia (amu unit) for *cjc(=o)ono*: 170.66, 780.45 and 949.24

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